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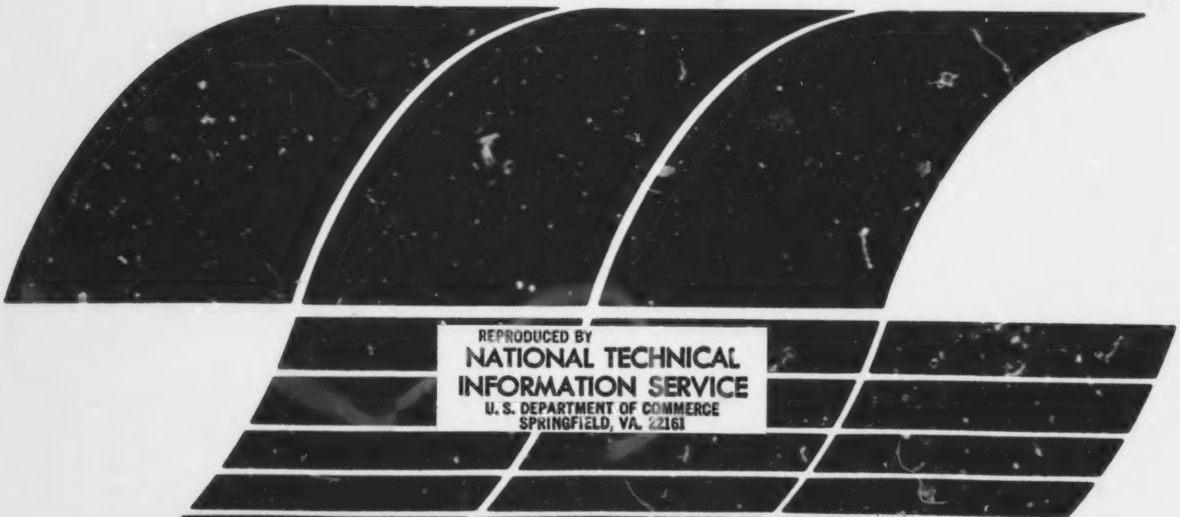
Interagency Energy/Environment R&D Program Report



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16. ABSTRACT The report gives results of a comparative multimedia assessment of coal- versus oil-firing in a controlled industrial boiler, to determine relative environmental, energy, economic, and societal impacts. Comprehensive sampling and analyses of gaseous, liquid, and solid emissions from the boiler and its control equipment were conducted to identify criteria pollutants and other species. Major conclusions include: (1) While the quantity of particulates from oil-firing is considerably less than from coal-firing, the particles are generally smaller and more difficult to remove, and the concentration of particulates in the treated flue gas from oil-firing exceeded that from coal-firing. (2) NOx and CO emissions during coal-firing were about triple those during oil-firing. (3) Sulfate emissions from the boiler during coal-firing were about triple those during oil-firing; however, at the outlet of the control equipment, sulfate concentrations were essentially identical. (4) Most trace element emissions (except vanadium, cadmium, lead, cobalt, nickel, and copper) are higher during coal-firing. (5) Oil-firing produces cadmium burdens in vegetation approaching levels which are injurious to man; coal-firing may produce molybdenum levels which are injurious to cattle. (6) The assessment generally supports the national energy plan for increased use of coal by projecting that the environmental insult from coal-firing is not significantly different from that from oil-firing.

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Assessments	Carbon Monoxide	Stationary Sources	14B	
Boilers	Sulfates	Environmental Assessment	13A	
Combustion	Sulfur Oxides		21B	
Fuel Oil	Trace Elements	Industrial Boilers	21D	06A
Coal	Chemical Analysis	Particulate		07D
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C. Leavitt, K. Arledge, C. Shih,
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R. Beimer, G. Richard, and M. Yamada

TRW, Inc.
One Space Park
Redondo Beach, California 90278

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EPA Project Officer: Wade H. Ponder

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

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ABSTRACT

The report gives results of a comparative multimedia assessment of coal versus oil firing in a controlled industrial boiler. Relative environmental, energy, economic, and societal impacts were identified. Comprehensive sampling and analyses of gaseous, liquid, and solid emissions from the boiler and its control equipment were conducted to identify criteria pollutants and other species. Major conclusions include: (1) While the quantity of particulates from oil firing is considerably less than from coal firing, the particles are generally smaller and more difficult to remove, and the concentration of particulates in the treated flue gas from oil firing exceeded that from coal firing. (2) NO_x and CO emissions during coal firing were about triple those during oil firing. (3) Sulfate emissions from the boiler during coal firing were about triple those during oil firing; however, at the outlet of the control equipment, sulfate concentrations were essentially identical. (4) Most trace element emissions (except vanadium, cadmium, lead, cobalt, nickel, and copper) were higher during coal firing. (5) Oil firing produces cadmium burdens in vegetation approaching levels which are injurious to cattle. (6) The assessment generally supports the national energy plan for increased use of coal by projecting that the environmental insult from controlled coal firing is not significantly different from that from oil firing.

This report was submitted in fulfillment of Contract Number 68-02-2613, Task 8 by TRW Environmental Engineering Division under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from October 24, 1977 to May 5, 1978, and work was completed as of May 5, 1978.

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LIST OF ABBREVIATIONS

acm/min	Actual Cubic Meters Per Minute
ACFM	Actual Cubic Feet Per Minute
DSCM	Dry Standard Cubic Meters
ESCA	Electron Spectroscopy for Chemical Analyses
FGD	Flue Gas Desulfurization
ICPOES	Inductively Coupled Plasma Optical Emission Spectroscopy
MATE	Minimum Acute Toxicity Effluent
NAAQS	National Ambient Air Quality Standards
NSPS	New Source Performance Standards
SSMS	Spark Source Mass Spectrometry
TSP	Total Suspended Particulate

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SECTION I

INTRODUCTION

A comparative multimedia assessment of coal firing and oil firing in an industrial boiler was conducted. Extensive sampling and analysis of all major gaseous, liquid, and solid emissions and effluents was done. The test boiler was a dual fuel 10 MW equivalent unit that is capable of burning both coal and oil. During the tests conducted for this study the boiler burned either exclusively coal or oil, although it can burn both fuels simultaneously if required. The boiler is equipped with a pilot double-alkali flue gas desulfurization (FGD) unit designed to treat approximately 30% of the total flue gas, approximately 3 MW equivalent. During the tests, however, the FGD was processing only about 11-14% (13% average) of the total when coal was fired and 23-32% (25% average) when oil was burned. This corresponds to approximately 1.3 MW and 2.5 MW, respectively. Because the FGD was operating at less than design capacity, there is some question about the typicalness of the test results. That is, the pilot unit may have been performing better than full size commercial versions will.

The assessment consists of several parts. First, comprehensive emissions assessments of each fuel were conducted. These assessments consist of detailed examinations of gaseous, liquid and solid emissions and effluents considering both pre- and post-scrubber emissions for each fuel. The emissions to all three media were determined for the case where no FGD was present and for the case where an FGD capable of scrubbing 100% of the flue gas was present. The comprehensive emissions assessment also consisted of an examination of the effects and efficiencies of the scrubber for both fuels.

These comprehensive emissions assessments were used to develop a comparative emissions assessment. This assessment examines the differences in the quantities and character of the emissions resulting from the combustion of each fuel. In this case the primary emphasis was on the emissions and effluents resulting from the burning of each fuel where 100% scrubbing capacity was available. This part of the project was concerned with determining the emissions resulting from each fuel with emission

Comprehensive sampling and analyses of gaseous, liquid, & solid emissions from the boiler and its control equipment were conducted to identify criteria pollutants and other species.

controls in place. Of special concern was the cross-media impacts of each fuel.

On the basis of the emissions assessments a comparative environmental, societal and energy impact assessment was developed. The emphasis here was on the relative impacts of each fuel assuming full flue gas desulfurization. The uncertainties inherent in these types of analyses dictated that the differences in, rather than the absolute magnitude of these impacts, be considered.

The report consists of three volumes. Volume I is an Executive Summary which summarizes the major results and conclusions of the study. This volume, Volume II, presents the comparative assessments. Included are a description of the test setting, the comparative emissions assessment, and the comparative environmental societal and energy impact assessment. Volume III contains the comprehensive assessments and appendices and includes detailed descriptions of the test site, the test protocol and a detailed presentation of data.

SECTION 2

SUMMARY AND CONCLUSIONS

A comparative assessment of coal and oil firing in a controlled industrial boiler was conducted. The comprehensive emissions assessments for each fuel were used to develop a comparative emissions assessment. On the basis of the emissions assessment a comparative environmental assessment was developed.

The following is a list of the major conclusions resulting from the comparative and environmental assessments:

COMPARATIVE EMISSIONS ASSESSMENT

- Uncontrolled emissions of criteria pollutants produced during coal firing correspond well with emission factors from AP-42. This observation does not generally hold true for oil-fired emissions. NOx emissions from oil firing were nearly 23% lower than the AP-42 emission factor, although they appear to be within the normal range for similar industrial units. CO emissions from oil firing were nearly 63% lower than the AP-42 emission factor. Oil-fired SO_2 and total hydrocarbons correspond well with their respective AP-42 emission factors. Particulate emissions from oil firing, in the absence of coal ash contamination, are approximately twice the value tabulated in AP-42.

- NOx emissions increased with increasing load for both coal and oil firing, as expected. Available data indicate that for boiler loadings between 90 and 100%, NOx emissions from coal firing are approximately three times greater than from oil firing.

- Observed reductions of NOx emissions for coal firing and early oil firing tests appear to be due, at least in part, to air leakage into the scrubber outlet sampling line. Data from later oil firing tests, not known to be subject to leakage problems, indicate that NOx removal across the scrubber is on the order of 2%.

- Uncontrolled CO emissions from coal firing were 15.9 ng/J (0.04 lb/MM Btu) while those from oil firing were 5.47 ng/J (0.01 lb/MM Btu). This factor of three difference is at variance with AP-42 data indicating that CO emissions from oil firing are 23% lower than those from coal firing. Apparent reductions in CO emissions across the scrubber are not considered significant due to air leakage in the sampling train and the low sensitivity of analysis at the measured CO concentrations.

- Uncontrolled SO_2 emission rates during coal and oil firing were

1112 ng/J (2.59 lb/MM Btu) and 993 ng/J (2.31 lb/MM Btu), respectively. Removal data indicate an average scrubber removal efficiency of 97% during both coal and oil firing. Controlled SO_2 emissions for coal and oil firing were 36.3 ng/J (0.08 lb/MM Btu) and 26.8 ng/J (0.06 lb/MM Btu), respectively, which are lower than either existing or proposed NSPS limitations.

- Particulate loadings prior to scrubbing were 2951 ng/J (6.86 lb/MM Btu) during coal firing and 59.0 ng/J (0.14 lb/MM Btu) during oil firing, in the absence of coal ash contamination. Scrubbing removed 99% of the coal-fired particulates and 75% of the oil-fired particulates. The lower removal efficiency obtained during oil firing is attributed to the increased fraction of particles smaller than 3 μm; at least 21% of the uncontrolled oil-fired particulates are less than 3 μm while substantially less than 1% of uncontrolled coal-fired particulates are under 3 μm in diameter.

- There appears to be a net increase in emission rates across the scrubber for coal-fired particulates less than 3 μm in size. This net increase can be attributed to the poor removal efficiency of the scrubber for fine particulates, and to the sodium bisulfate ($NaHSO_4$) and calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) particulates generated by the scrubber. Both $NaHSO_4$ and $CaSO_3 \cdot 1/2\ H_2O$ have been identified at the scrubber outlet but not at the inlet. Although a very slight increase in oil-fired particulates in the 1-3 μm range was observed, a net decrease in particulates less than 3 μm was observed during oil firing. Based on the results of coal firing tests, it appears reasonable that scrubber generated particulates were present in the scrubber outlet stream during oil firing but that the high fine particulate loading associated with oil firing masked detection of these materials.

- Of the 22 major trace elements analyzed in the flue gas stream during coal firing, 18 exceed their MATE values at the scrubber inlet and 4 at the scrubber outlet. Similarly, for oil firing, 11 exceeded their MATE values at the scrubber inlet while 5 exceeded their MATE values at the scrubber outlet. Elements exceeding their MATE values at the scrubber outlet and which are common to both fuels are arsenic, chromium and nickel. Additionally, iron exceeded its MATE value at the scrubber outlet during coal firing as did cadmium and vanadium during oil firing. The overall removal of trace elements across the scrubber is 99% for coal firing and 87% for oil firing.

- Polycyclic organic material (POM) was not found in the scrubber inlet or outlet at detection limits of 0.3 $\mu g/m^3$ for either coal or oil firing. MATE values for most POM's are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)pyrene and dibenz(a,h)anthracene - are less than 0.3 $\mu g/m^3$, additional GC/MS analyses at higher sensitivity would be required to conclusively preclude the presence of all POM's at MATE levels.

- Beryllium emissions after scrubbing were less than or equal to its MATE value for coal and oil firing. At the measured emission concentrations, the National Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would only be exceeded by boilers of 50 MW capacity for coal firing and 100 MW capacity for oil firing.

- The combined waste water stream from the boiler operation may not pose an environmental hazard in terms of organic materials since the discharge concentrations of organics are well below their MATE values for both coal and oil firing. The same conclusion may be drawn for inorganic compounds with the exception of cobalt, nickel, copper and cadmium for coal firing, and nickel and copper for oil firing, since these metals may exceed their MATE values.

- Organic emissions for coal and oil firing were very similar. Total organic emissions were less than 9 ng/J (0.02 lb/MM Btu) for both tests, and these emissions appear to be primarily C_1 to C_6 hydrocarbons and organics heavier then C_{16}. While uncontrolled emission rates for both coal and oil firing are low, emissions of these organics were further reduced by about 85% in the scrubber unit.

- The organic compounds identified in the gas samples from both coal and oil firing were generally not representative of combustion-generated organic materials, but were compounds associated with materials used in the sampling equipment and in various analytical procedures. This again confirms the low level of organic emissions.

- The relatively poor removal efficiency (approximately 30% in both oil and coal-fired tests) for SO_3 across the scrubber is an indication that SO_3 is either present as very fine aerosols in the scrubber inlet, or is converted to very fine aerosols in the flue gas stream as it is rapidly cooled inside the scrubber.

- The fraction of fuel sulfur converted to SO_3 during oil firing was 50 to 75% higher than during coal firing. In contrast, the fraction of fuel sulfur converted to sulfates during coal firing was twice that during oil firing.

- Sulfates are more efficiently removed than SO_3 (60% removal for oil firing and 88% for coal firing). This indicated that $SO_4^=$ is probably associated with the larger particulates which are more efficiently removed than smaller particulates. The higher sulfate removal from the coal flue gases is explained by the higher particulate loading during coal firing.

- Uncontrolled chloride and fluoride loadings were higher during coal firing (5 and 0.2 ng/J, respectively) than during oil firing (0.2 and 0.02 ng/J, respectively). This was attributed, in the case of chlorides, to a higher fuel chlorine content for coal than for oil. Chlorides were removed with better than 99% efficiency from coal flue gases and with about 51% efficiency from oil flue gases. This difference was attributed to the higher particulate removal efficiency for coal particulates. Fluorides were removed with greater than 86% and about 87% efficiency for coal and oil firing, respectively. Uncontrolled nitrate emissions were 0.08 ng/J during oil firing, and nitrates were removed from oil flue gases with 57% efficiency.

- The scrubber cake produced during coal firing contained 29% coal fly ash; during oil firing it contained 1% oil fly ash. The trace element concentrations in the coal-fired scrubber cake exceeded their health based MATE values, with the exception of boron. In the oil-fired scrubber cake, all trace elements except antimony, boron, molybdenum and zinc exceeded their health based MATE values. All ecology based MATE values were exceeded by trace element concentrations during both oil and coal firing. Because the trace elements may leach from the disposed scrubber cake, these solid wastes must be disposed of in specially designed landfills.

COMPARATIVE ENVIRONMENTAL ASSESSMENT

- The difference in environmental insult expected to result between coal and oil combustion emissions from a *single* controlled 10 MW industrial boiler is insignificant. This is because: 1) there are only slight differences in the emissions levels of the pollutants, or 2) the absolute impact of either fuel use is insignificant.

- The environmental impacts of emissions from a *cluster* of controlled 10 MW industrial boilers are potentially significant. The impacts include health effects, material damages, and ecological effects from high levels of SO_2, NOx and suspended particulate matter; health effects and ecological damage due to trace metal accumulation in soils and plants; and aesthetic degradation from visibility reduction and waste disposal sites.

- The risk of environmental damage from emissions of controlled industrial boilers, whether oil or coal-fired, is considerably less than the risk posed by emissions from uncontrolled industrial boilers. It should be noted that this finding is based on an exceptional facility. The reference facility is very well run and maintained, and emissions are low.

- The environmental acceptability of a cluster of controlled industrial boiler emissions is more dependent on site specific factors (e.g., background pollution levels, location and number of other sources) than type of fuel utilized. Careful control of the site specific factors can avert potential environmental damages and generally compensate for any differential effects arising between the use of coal or oil.

- With the possible exception of ambient levels of NO, the risk of violating the NAAQS due to operation of clusters of controlled industrial boilers is essentially the same whether the fuel combusted is coal or oil. Based on tests of the reference 10 MW boiler (which was not controlled for NOx emissions), localized NOx concentrations produced by coal firing are estimated to be twice the level of that resulting from oil firing, and greater than the levels permitted by the NAAQS for 24-hour and one year averaging periods.

- Short term (3 hour and 24 hour averaging times) maximum ambient concentrations present the most significant air pollution problem resulting from operation of controlled industrial boilers. Restrictions imposed by the NAAQS for short term ambient levels would be most constraining to boiler operation in areas where air quality is already only marginally acceptable. Expected long term concentrations arising from boiler emissions would not appear to pose a risk for violation of the NAAQS.

- Coal firing appears to produce a greater enrichment of trace elements in the flue gas desulfurization cake than oil firing produces. However, the scrubber cake resulting from either coal or oil firing contains sufficient amounts of heavy metals and toxic substances to pose difficult waste disposal problems.

The impact categories considered include public health, ecology, societal, economic, and energy. The specific findings with respect to the various impact categories are summarized briefly below.

Health Effects--

- Based on the Lundy/Grahn Model for health effects associated with suspended sulfate levels, regional emissions levels from controlled oil or coal-fired industrial boilers would not be expected to cause a significant impact on regional health. Emissions from uncontrolled boilers would result in substantially greater levels of regional suspended sulfate levels, and the associated health effects would be an order of magnitude greater.

- Emissions from clusters of controlled industrial boilers are expected to cause significant adverse health effects in a localized area near the plant cluster. Oil firing would be expected to result in localized health effects about one third less severe than those resulting from coal firing. The increase in mortality attributable to either controlled coal or oil firing is appreciably less than that associated with uncontrolled industrial boilers emitting higher levels of particulates and SOx.

- The impact of solid waste generation on health is essentially the same for controlled coal firing and oil firing, provided suitable land disposal techniques are employed to assure minimal leaching rates and migration of trace elements to groundwater and the terrestrial environment.

- Addition of cadmium to a localized environment in the quantities produced by clusters of controlled industrial boilers may result in cadmium concentrations in plants approaching levels injurious to man. Because cigarettes contain significant cadmium levels, smokers are more apt to achieve thresholds of observable symptoms for cadmium exposure when consuming additional cadmium via the food chain.

- The concentration of metals in runoff waters due to controlled oil firing is predicted to be slightly less than that occurring from controlled coal firing; in either case, hazard to human health by drinking water is remote.

- Trace element emissions from clusters of controlled industrial boilers may significantly increase local background levels in drinking water, plant tissue, soil, and the atmosphere; however, the expected increases in the levels of such elements are generally several orders of magnitude less than allowable exposure levels. Oil firing is estimated to cause cadmium burdens in plants approaching levels injurious to man, and coal firing may produce plant concentrations of molybdenum which are injurious to cattle.

Ecology--

- The potential for crop damage from either controlled coal firing or oil firing depends greatly on ambient levels of NOx, SO_2, or trace element soil concentrations. If such levels are presently high, localized plant damage would be expected to occur within a 1 to 2 km range from a controlled boiler cluster. Leaf destruction from SO2 exposure would be expected to be slightly more severe in the vicinity of a cluster of controlled boilers which are coal-fired as opposed to oil-fired. For boilers uncontrolled for NOx emissions, plant damage would be expected to be significantly greater in the vicinity of the coal-fired cluster, owing to higher levels of ambient NOx produced. The likelihood of damage occurring in plants due to emissions of trace elements from either controlled oil or coal firing is remote, with the possible exception of injury due to elevated levels of molybdenum and cadmium in plant tissue resulting from coal firing and oil firing, respectively.

- The effect of emissions from industrial boilers on trace element burdens in plants is greater via soil uptake than by foliar interception. This is because soil concentrations are the result of accumulative long term exposure to boiler emissions whereas foliar exposure is determined by the immediate deposition rate of emissions on the plant surface and the lifetime of the leaf.

- The impact of fossil fuel combustion in controlled oil or coal-fired boilers on plant damage via acid precipitation would be insignificant. The levels of suspended sulfate (the origin of acid rain) would be essentially the same whether the controlled boilers are coal or oil-fired.

- Measurement and analyses of leaching rates at experimental waste disposal sites indicate that landfills of untreated flue gas desulfurization system scrubber cake can be constructed such that significant adverse impacts will not occur.

Societal--

- The impact of boiler emissions on corrosion in the local area near a cluster of controlled industrial boilers would be significant. The corrosion rate would be slightly greater when the boilers are coal-fired. However, the extent of this overall impact (oil or coal) is minor compared to that which occurs when industrial boilers are uncontrolled.

- The increase in annual TSP and soiling damages in the vicinity of a cluster of controlled industrial boilers could result in additional cleaning and maintenance costs about 10 to 15% greater than that already experienced in a typical urban area. The cleaning costs may be slightly greater when the boilers are coal-fired.

- Emissions of particulate matter from controlled industrial boilers may result in visibility reduction. This aesthetic degradation would occur in a localized area near the boiler cluster, and would occur to essentially the same extent whether the boilers are oil or coal fired.

- Total land disposal requirements for scrubber cake waste generated by controlled coal firing are three times greater than those for controlled oil firing. Waste disposal of the scrubber wastes may result in significant depreciation of property value and aesthetic degradation in the area of the disposal site. These impacts would be more severe if boilers use coal rather than oil.

Economic--

- The differential direct economic impact between emissions from coal firing and oil firing is generally insignificant with the possible exception of some differences occurring in a limited localized area near clusters of boilers. The extent of the incremental direct economic impacts is proportional to the extent of the incremental environmental damages.

- Differential second order economic impacts, such as changes in hospital employment, alteration of taxes, or changes in income, are expected to be insignificant between emissions from controlled oil and coal-fired industrial boilers

Energy--

- At the present time, the comparative assessment of the effects of emissions from controlled oil and coal-fired industrial boilers tends to support the national energy plan for intensified utilization of coal. The fuel choice of oil or coal is a relatively minor issue concerning the environmental acceptability of controlled industrial boilers; other site specific and plant design factors exert a greater effect on environmental damages. While it was shown that fuel choice caused significant differences in impacts to occur when the boiler is uncontrolled for NOx emissions, these differences may be mitigated by the addition of NOx control technologies with minimal overall cost impact.

- As concern for environmental protection increases, the issue may not be whether coal or oil use is more environmentally acceptable, but whether the increasing use of fossil fuels can be continued at the present levels of control technology without potential long-term damages. If it is found that long-term effects of pollution (e.g., trace metals accumulation, lake acidity from acid rains) from fossil fuel combustion and other sources are environmentally unacceptable, it is clear that energy use may be affected. Energy cost will increase with increasing control requirements, possibly to the level where other cleaner forms of energy become more competitive.

SECTION 3

TEST SETTING

The host for this assessment was the Pottstown, Pennsylvania plant of the Firestone Tire and Rubber Company. Boiler No. 4, one of four used to supply process steam to the plant, was tested. The boiler burns either coal or oil and has a pilot FMC double alkali flue gas desulfurization system designed to treat approximately one-third of the boiler's flue gas.

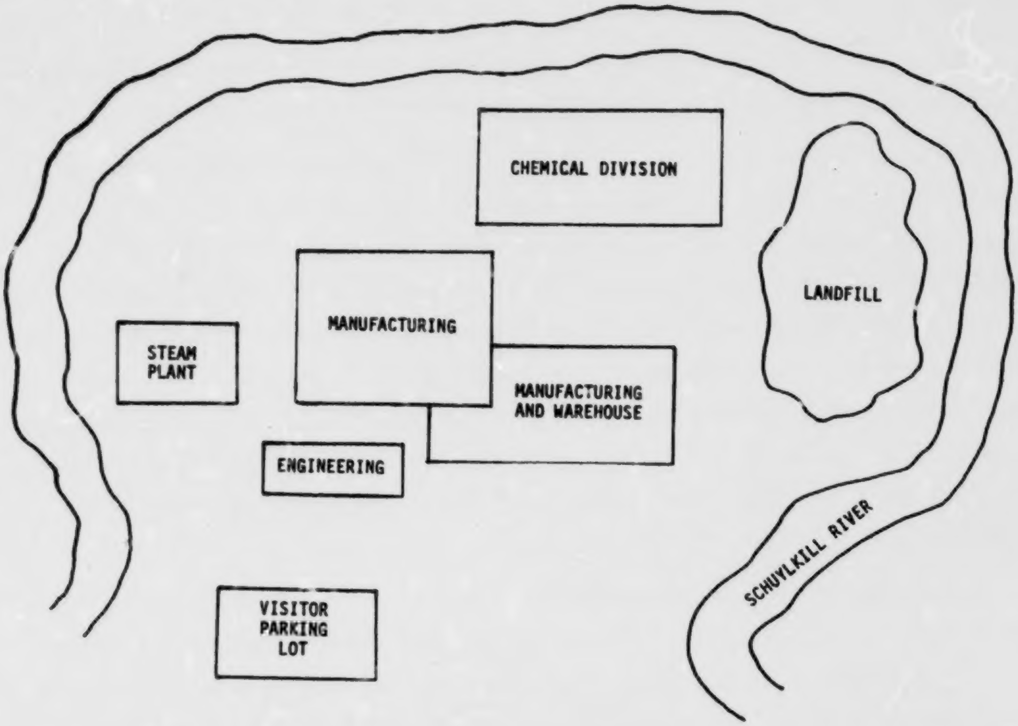
The excellent cooperation and assistance from the Firestone Tire and Rubber Company and FMC was invaluable in performing this assessment.

The test boiler (No. 4) is one of four comprising a steam plant which supplies process steam and heating steam for the facility. The boiler is one of three which operates at a fairly constant rate of 45,400 kg/hr (100,000 lb/hr) of steam. Process steam demand is relatively steady, since the plant operates 24 hours per day, seven days per week. Fluctuations in heating load are satisfied by either boosting steam generation rates on these boilers or by operating the fourth boiler (No. 1). The steam generation rate of Boiler No. 1 varies from zero to approximately 22,700 kg/hr (50,000 lb/hr) of steam. A schematic of the steam plant is shown in Figure 3-1.

Boiler No. 4 is a once-through Babcock and Wilcox Type P-22 EL integral furnace. Installed in 1958 and originally designed as a coal-fired unit, it was converted to fire either coal or fuel oil in 1967. The changeover from one fuel to the other can be accomplished in less than thirty minutes. (See Section 3, Volume III of this report for additional detail.)

The two fuels are usually not burned simultaneously except when converting from oil to coal firing. The coal is ignited by continuing oil firing until a stable coal flame is obtained. Oil and coal can be fired simulataneously to maintain acceptable steam generation rates if coal with a low heat content is burned.

The boiler uses either Number 6 fuel oil or Eastern bituminous coal. Currently there are no fuel oil specifications. Therefore, sulfur and heat content of the oil vary with supplier. The coal is required to meet CLASS II, Group 2 of ASTM D388. Normally the coal used is mined in Pennsylvania.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ENGINEERING
SCHUYLKILL RIVER
VISITOR PARKING LOT

Figure 3-1. Industrial site plant layout.

However, coal was purchased from a mine in Kentucky during the 1978 coal strike.

An air preheater is located in the flue gas plenum directly downstream of the boiler. This gas-to-gas heat exchange recovers approximately 4.2 gigajoules/hr (4 million BTU/hr) when the boiler is operating at full load.

EXHAUST GAS CLEANING

The flue gases are treated by an air pollution control system. The air pollution control equipment consists of multiclone units and a pilot FGD unit. All of the flue gas passes through the multiclones. The stream then is split and two-thirds of the flue gas ducted to the stack. The other one-third is ducted to the pilot FGD system. The boiler has no NO_x controls.

The characteristics and volume of fly-ash collected by the multiclone unit vary significantly depending upon the type and composition of the fuel. During oil firing, very little fly-ash leaves the boiler. During coal firing, a large amount reaches the multiclones.

The collection efficiency of the multiclone varies as a function of the particle size distribution and grain loading. Typically, multiclones remove 90% of those particles with diameters 10μ and greater, and 50% to 80% of those particles with diameters 3μ and greater. The collection efficiency of multiclones drops off rapidly for particles less than 3μ diameter.

Fly-ash is periodically removed and transported to an on-site landfill for final disposal.

FLUE GAS DESULFURIZATION SYSTEM

The flue gas desulfurization (FGD) system was designed and manufactured by FMC Corporation. The FGD system is a pilot unit designed to handle 280 acm/min (10,000 ACFM) of flue gas, which is approximately one-third of the volume of the flue gas produced by the boiler.

Figure 3-2 is the basic flow diagram of the FMC FGD system as it is applied at this site.

The flue gas (Stream 1) is withdrawn downstream of the boiler on the exit side of the multiclone dust collectors. During oil firing the particulate loading to the scrubber is low. During coal firing the multiclones

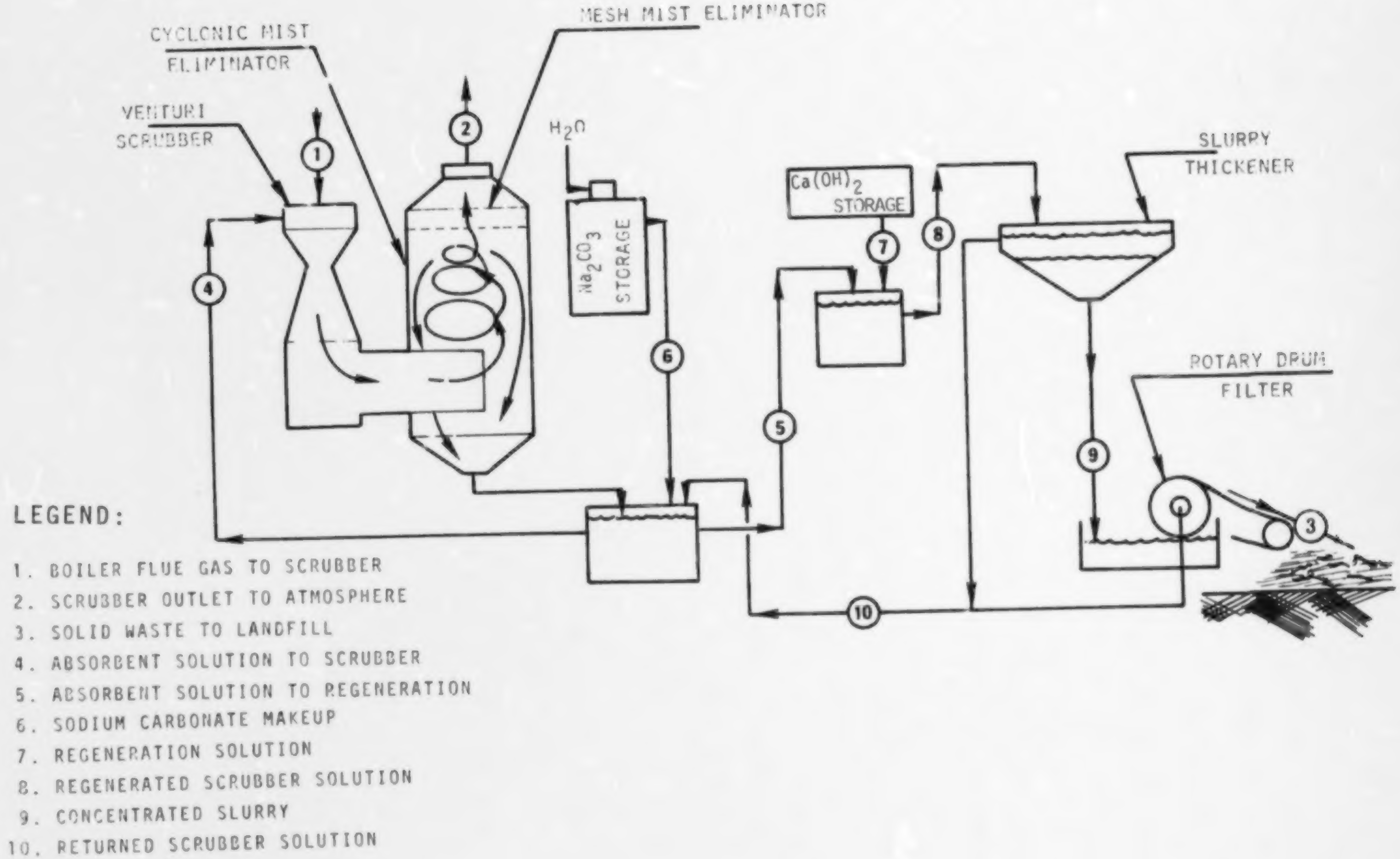
CYCLONIC MIST ELIMINATOR
MESH MIST ELIMINATOR
VENTURI SCRUBBER
H_2O
Na_2CO_3 STORAGE
$Ca(OH)_2$ STORAGE
SLURRY THICKENER
ROTARY DRUM FILTER
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
LEGEND:
1. BOILER FLUE GAS TO SCRUBBER
2. SCRUBBER OUTLET TO ATMOSPHERE
3. SOLID WASTE TO LANDFILL
4. ABSORBENT SOLUTION TO SCRUBBER
5. ABSORBENT SOLUTION TO REGENERATION
6. SODIUM CARBONATE MAKEUP
7. REGENERATION SOLUTION
8. REGENERATED SCRUBBER SOLUTION
9. CONCENTRATED SLURRY
10. RETURNED SCRUBBER SOLUTION

Figure 3-2. Flow diagram of the FMC flue gas desulfurization unit.

do not achieve complete fly-ash removal. Therefore, the fly-ash loading in the gas stream inlet to the scrubber is substantially higher than during oil-firing. The FGD system was designed to operate with or without fly-ash, and can be operated without any mechanical changes on either fuel.

Upon entering the FGD unit the flue gases are contacted with a slightly acidic scrubbing solution (stream 4) and the sulfur dioxide is absorbed. The process utilizes a sodium sulfite-sodium bisulfite solution as the absorbent. The particulate matter and sulfur dioxide are removed at the scrubber throat and carried away in the scrubbing solution.

A bleed stream (stream 5) of the scrubbing solution is removed from the system at a rate which will keep the pH of the solution in an acceptable range. The bleed stream is reacted with calcium hydroxide in a short retention time, agitated vessel to regenerate the sodium sulfite.

The slurry of precipitated sulfur compounds (stream 8) is concentrated and then pumped to a rotary drum filter where the essentially clear liquid and solid waste products are separated. The clear liquid (stream 10) is returned to the system for further utilization. The solid wastes, in the form of filter cake containing 40% (by weight) water (stream 3), are removed from the rotary drum filter and conveyed to a storage bin to await transportation to the dump site. Because of the heavy particulate loading, more filter cake is produced during coal firing than during oil firing.

The on-site landfill, which is the final disposal facility for all of the solid waste generated at the facility, has several test wells from which samples are collected every three months and sent to an independent laboratory for analysis. In addition, monthly tests are conducted by plant personnel to monitor sodium and specific conductivity. With permission of the Pennsylvania Department of Environmental Resources, this site is being used as an experimental disposal area for the filter cake from the FMC unit.

BOILER BLOWDOWN

There are two blowdown sources in the boiler system: the steam drum and the mud drum. There is a continuous blowdown from the steam drum which keeps the level of suspended solids in the boiler feedwater within an acceptable range. Tests of the steam drum blowdown effluent are made every four hours and adjustments to blowdown rate are made accordingly. The mud drum is blown once per shift.

The effluent from both blowdowns is sent to the same pit that collects effluent from the water pretreatment unit.

TEST DESCRIPTION

Multi-media emission tests were conducted on Boiler No. 4 of the Firestone Plant from 27 September through 8 October 1977. Solid, liquid and gaseous emission streams were sampled during coal firing and during oil firing to obtain data for the assessments. Flue gas sampling was conducted before and after the pilot flue gas desulfurization unit to establish which pollutants are removed, modified, or produced by the control device.

Emissions were characterized using EPA's phased approach to sampling and analysis. This approach utilizes two separate levels of sampling and analytical effort (Level 1 and Level 2). Level 1 is a sampling and analysis procedure accurate within a factor of about 3. This level provides preliminary assessment data and identified problem areas and information gaps which are then used to form the Level 2 sampling and analysis effort. Level 2 provides more accurate detailed information that confirms and expands the information gathered in Level 1. The methods and procedures used for Level 1 sampling and analysis are documented in the manual, "Combustion Source Assessment Methods and Procedures Manual for Sampling and Analysis", September 1977. The Level 2 methods and procedures included "state-of-the-art" techniques as adapted to the needs of this site. They are delineated in Volume III Appendices B and C.

Normally all Level 1 samples are analyzed and evaluated before moving to Level 2. Because of program time constraints, the Level 1 and Level 2 samples were obtained during the same test period. However, analysis of the samples did proceed in a phased manner except where sample degradation was of concern. In those cases, Level 2 analyses were performed on the samples prior to completion of Level 1 analyses.

The industrial boiler assessment tests were conducted during both coal and oil firing. Figure 3-3, the system schematic for Boiler No. 4, includes

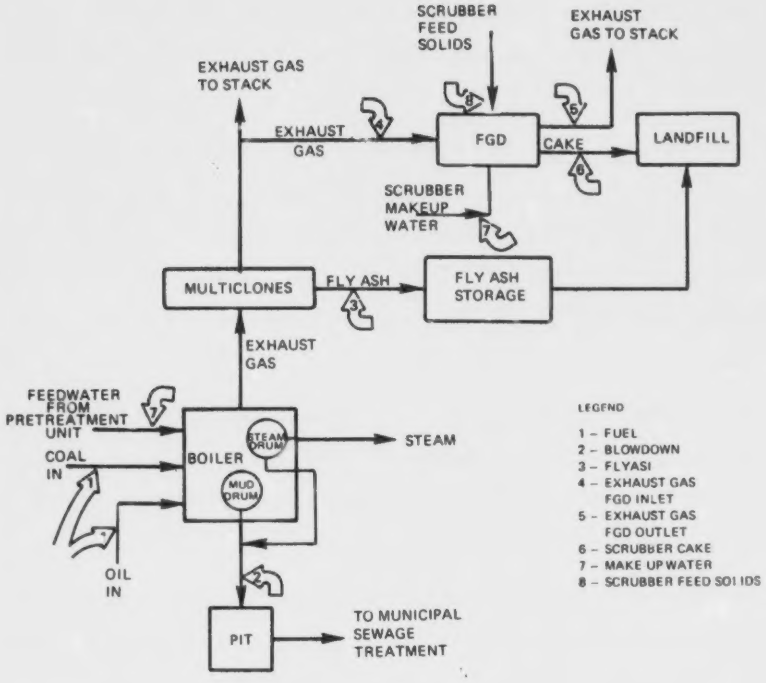
SCRUBBER
FEED
SOLIDS
EXHAUST
GAS TO STACK
EXHAUST GAS
TO STACK
EXHAUST
GAS
FGD
CAKE
LANDFILL
SCRUBBER
MAKEUP
WATER
MULTICLONES
FLY ASH
FLY ASH
STORAGE
EXHAUST
GAS
FEEDWATER
FROM
PRETREATMENT
UNIT
COAL
IN
BOILER
STEAM
DRUM
MUD
DRUM
STEAM
OIL
IN
PIT
TO MUNICIPAL
SEWAGE
TREATMENT
1
2
3
4
5
6
7
7
8
LEGEND
1 – FUEL
2 – BLOWDOWN
3 – FLYASH
4 – EXHAUST GAS
FGD INLET
5 – EXHAUST GAS
FGD OUTLET
6 – SCRUBBER CAKE
7 – MAKE UP WATER
8 – SCRUBBER FEED SOLIDS

Figure 3-3. Boiler system schematic and sampling locations.

the pilot flue gas desulfurization unit and shows all sample locations. Parameters sampled during coal and oil firing at each location are summarized in Table 3-1. The table also identifies the sampling and analysis method used to characterize each parameter. Volume III contains a more complete description of the sampling and analysis activities.

The boiler exhaust gas was sampled at the inlet and outlet of the desulfurization unit. Integrated bag samples were taken at both points in each test.

Continuous monitors for CO, NO/NO_x, SO_2, and total hydrocarbons (as CH_4) were installed in the system as shown in Figure 3-4 and operated during all tests. A Thermal Electron Corporation (TECO) gas conditioner was used to remove condensate and particulate from the flue gas prior to entering the CO, NO_x, and SO_2 analyzers. Model numbers for all analyzers are shown in Table 3-1.

The Source Assessment Sampling System (SASS) was used to collect both gaseous and particulate emission samples at the inlet and outlet for Level 1 organic and inorganic analysis. The train was run for 6 to 8 hours until a minimum of 30 cubic meters of gas had been collected.

Previous sampling and analysis efforts had indicated possible interference of SASS train materials on certain organic and inorganic analysis when at the lower detection limits of Level 2 methods. To avoid this possibility, all glass sampling trains were used to collect Level 2 samples. Two Method 5 sampling trains were modified for Level 2 organic and inorganic sample acquisition. Both trains sample approximately 10 cubic meters of flue gas during a 6- to 8-hour run time. The Level 2 trains were run at the inlet and outlet of the FGD unit for both coal and oil firing.

A controlled condensate train (Goksoyr-Ross) was used at each location during coal and oil firing to obtain samples for SO_2, SO_3 (as H_2SO_4), particulate sulfate, HCl and HF.

During Level 2 test runs, Anderson Cascade impactors were used to obtain particulate samples by particle size fraction.

TABLE 3-1. PARAMETERS SAMPLED FOR COAL AND OIL FIRING

Location	Parameter	Sampling Method	Analysis
1	FUEL (coal & oil)	Grab	
	C, H, N, S, ash, moisture, heating value		Ultimate (lab)
	inorganics		Level II (lab)
2	COMBINED BLOWDOWN	Composite dipper	On-site HACH kit
	alkalinity/acidity		
	pH		
	conductivity		
	hardness		
	TSS		
	nitrate		
	sulfate		
	sulfite		
	phosphate		
	ammonia		
	nitrogen		
	organics		Level 1 & 2 (lab)
3	FLYASH	Composite grab	
	inorganics		Level 1 & 2 (lab)
	organics		Level 1 & 2 (lab)
4 & 5	FLUE GAS (inlet & outlet)		
	CO	Continuous, Beckman Model 865	Direct reading
		Grab (bag)	GC (TCD) on site
	CO_2	Grab (bag)	GC (TCD) on site
	$NO/NO_2/NO_x$	Continuous, TECO	Direct reading
	N_2,O_2	Model 10A	GC (TCD) on site
		Grab (bag)	
	SO_2	Continuous, TECO	Direct reading
	SO_2/SO_3	Model 41	
	H_2SO_4 HCl HF	Goksoyr-Ross	Level 2 (lab)
	particulate sulfate		
	total hydrocarbons (as CH_4)	Continuous, Beckman Model 400	Direct reading
	C_1 - C_6 Organics	Grab (bag)	GC (FID) on site
		SASS	Level 1 (lab)
	particulate and vapor	Method 5	Level 2 (lab)
	particulate sizing	Anderson impactor	Level 2
		SASS	Level 1

(continued)

TABLE 3-1. (Continued)

Location	Parameter	Sampling Method	Analysis
6	SCRUBBER CAKE	Composite grab	
	inorganics		Level 1 & 2 (lab)
	organics		Level 1 & 2 (lab)
7	BOILER AND SCRUBBER MAKEUP WATER	Top grab	
	organics		Level 1 (lab)
	inorganics		Not required
8	SCRUBBER MAKEUP SOLIDS	Grab	Not required

The combined boiler blowdown was sampled using the composite dipper method. Boiler and scrubber makeup water were sampled by the top grab method. Samples from each location received the analyses shown in Table 3-1 for combined blowdown. In addition, samples from each location were extracted with methylene chloride and returned to the lab for further analysis.

Composite samples of the fly-ash and scrubber filter cake were collected per Level 1 procedures and returned to the lab for analysis. Grab samples of the scrubber feed solids were also obtained.

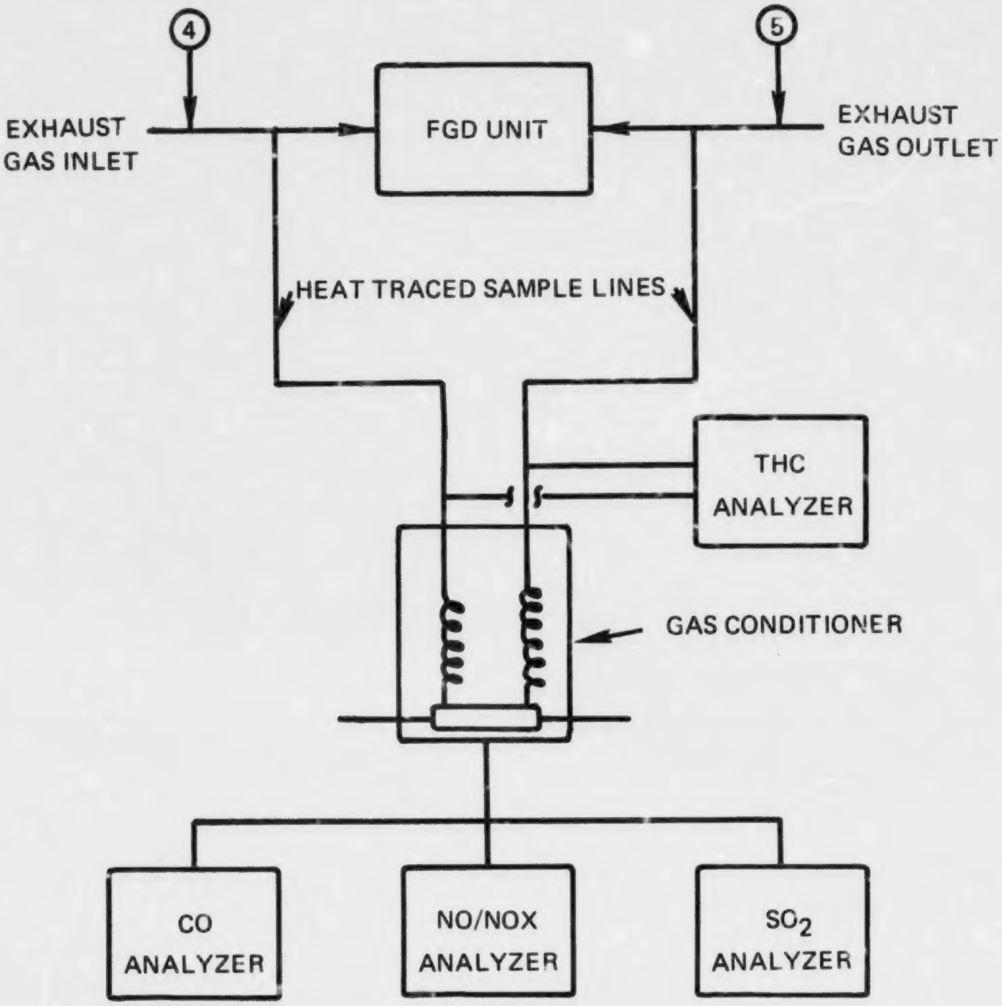
4
5
EXHAUST GAS INLET
FGD UNIT
EXHAUST GAS OUTLET
HEAT TRACED SAMPLE LINES
THC ANALYZER
GAS CONDITIONER
CO ANALYZER
NO/NOX ANALYZER
SO2 ANALYZER

Figure 3-4. Flue gas continuous monitor setup.

SECTION 4

COMPARATIVE ASSESSMENT OF COAL AND OIL FIRING CASES FOR AN INDUSTRIAL BOILER

This section provides a comprehensive multimedia assessment and comparison of emissions/effluents associated with coal and oil firing in an industrial boiler equipped with an FGD system. Data from Level 1/ Level 2 sampling and analyses were utilized to quantitatively determine and compare emissions in gas, solid and liquid waste streams generated during coal and oil firing. The performance of pollution control equipment during coal and oil firing was evaluated. Waste stream pollutant concentrations during coal and oil firing are compared with Minimum Acute Toxicity Effluent (MATE) values, when appropriate, to provide an indication of risk to public health and ecology. Simplified air quality models were used to determine the relative ground level air quality resulting from uncontrolled and controlled emissions from both fuels.

TEST CONDITIONS

Five tests were performed on the industrial boiler at Firestone for each of two fuels, a high volatile bituminous coal and a Number 6 fuel oil. Unit loading ranged from 31,800 to 45,400 kg steam per hour (70,000 to 100,000 pounds per hour) which corresponds to between 70 and 100% of full load operation for this boiler. Specific test conditions for both fuels are summarized in Table 4-1. Tabulated fuel feed rates are nominal, although their accuracies have been estimated from fuel analyses and steam production data under the assumption of 90% thermal efficiency. Nominal coal feed rates appear to be accurate to within 13%, while oil feed rates are accurate to approximately 3%. Oxygen concentrations presented in Table 4-1 were measured in flue gas samples drawn from the inlet of the system's wet scrubber unit. Due to air leakage into upstream ducting operating at sub-atmospheric pressure and possibly air leakage into the flue gas bag sampling system, tabulated oxygen concentrations are not necessarily representative of concentrations at the furnace outlet. Oxygen concentrations of 3 to 4% in the furnace after combustion are typical for this unit during normal operation; this concentration range corresponds to an excess air input of approximately 16 to 25%. Excess air estimates presented

TABLE 4-1. SUMMARY OF TEST CONDITIONS

Test No.	Steam Production Rate kg steam/hr	Steam Production Rate lbs. steam/hr	% of Maximum Load	Nominal Fuel Feed Rate, kg/hr	Nominal Fuel Feed Rate, gal/hr	% O_2 at Scrubber Inlet*	Estimated % Excess Air to Furnace†
COAL FIRING							
200	39,700	87,500	87.5	3629		7.8	20
201-1	44,200	97,500	97.5	3629		8.2	20
201-2	43,100	95,000	95.0	3629		8.4	20
201-3	34,000	75,000	75.0	3175		8.3	20
201-4	40,800	90,000	90.0	3629		6.7	20
OIL FIRING							
202-1	45,400	100,000	100		900	5.8	21
202-2	45,400	100,000	100		900	6.3	21
202-3	44,200	97,500	97.5		880	6.1	21
202-4	42,200	93,000	93.0		805	4.0	21
203	31,800	70,000	70.0		600	Not Measured	21

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*Due to air leaks in ducting upstream of the scrubber inlet, tabulated O_2 values are not representative of combustion zone O_2 concentrations. Combustion zone O_2 concentrations normally range from 3 to 4% for this unit.

†% excess air is estimated to be $100 \times \frac{O_2 - CO/2}{0.264\ N_2 - (O_2 - CO/2)}$, where O_2 was assumed to be 3.5% and other species concentrations were computed from fuel analyses.

in the table were computed assuming an average oxygen concentration of 3.5% in the furnace after combustion and utilizing ultimate analysis of the respective fuels.

Test data relating to flue gas flow rates and scrubber loading are summarized in Table 4-2. Flue gas flow rates measured at the scrubber inlet (expressed as dry standard cubic meters per minute, or dscm/min) are presented in the first column. For discussion in this report, standard temperature and pressure are defined as 20°C and one atmosphere, respectively. Typical inlet and outlet gas temperatures for the scrubber unit were 300°F and 125°F, respectively. Measured flow rates correspond to the scrubber loading listed in the second column of the table. An average scrubber loading of 96 dscm/min or 54% of design load was maintained during coal firing while a load of 180 dscm/min or 102% of design load was maintained during oil firing. Differences in scrubber loading for the two fuels are due to multiclone malfunction during the test period which resulted in an unusually high particulate loading at the scrubber inlet during coal firing. This high particulate loading increased the scrubber cake production rate per unit volume of flue gas processed and, owing to fixed capacity scrubber cake disposal facilities, necessitated a reduction in scrubber loading during coal firing.

Total flue gas flow rates presented in Table 4-2 were computed from fuel analyses, fuel feed rate data and flue gas oxygen analyses utilizing the following expression:

$$n_{FG} = \frac{4.762\ (n_C + n_S) + .9405\ n_H - 3.762\ n_{O_2}}{1 - 4.762\ (O_2/100)}$$

where:

n_{FG} = gm moles of dry effluent/gm of fuel.

n_j = gm moles of element j in fuel per gm of fuel.

O_2 = volumetric O_2 concentration in percent.

TABLE 4-2. FRACTION OF FLUE GAS PROCESSED BY THE SCRUBBER DURING EACH TEST

Test No.	Flow Rate at Scrubber Inlet, dscm/min*	% of Design Load	Total Flue Gas Flow Rate, dscm/min*	Fraction of Total Flue Gas Processed by the Scrubber
		COAL FIRING		
200	99	56	754	0.13
201-1	91	51	761	0.12
201-2	89	50	798	0.11
201-3	98	55	684	0.14
201-4	102	58	706	0.14
Average	96	54	741	0.13
		OIL FIRING		
202-1	193	109	824	0.24
202-2	192	109	850	0.23
202-3	189	108	818	0.23
202-4	155	88	657	0.24
203	171	97	537	0.32
Average	180	102	737	0.25

*Dry standard cubic meters per minute (dscm/min).

The scrubber is a pilot unit and, as such, was not sized to process the entire flue gas output of the furnace. As indicated in Table 4-2, the slipstream drawn for scrubber processing represented from 11 to 32% of the total flue gas generated.

Ultimate analyses of the feed coal and oil, averaged over the five tests run with each fuel, are presented in Table 4-3, along with standard deviations associated with averaging. The fuel compositions were essentially constant during the testing. The oil heat content is about 40% higher for oil than for coal, 40,741 vs 29,485 kJ/kg. To compare ash, sulfur, and nitrogen concentrations for the two fuels, these values are normalized to a weight per heat content basis, yielding 3360 ng ash/J for coal vs 4.9 ng ash/J for oil, 556 ng S/J for coal vs 481 ng S/J for oil, and 312 ng N/J for coal vs 88 ng N/J for oil. Laboratory tests have shown that 30 to 60% of the fuel nitrogen may be expected to be emitted as NO_x, as is discussed later (Reference 1).

Additional analyses were performed on fuel samples from tests 201-1 (coal) and 202-4 (oil) to determine concentrations of 20 trace elements (Ca, Mg, Sb, As, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, V, Zn, Se, Sr, Zr, Be, and Hg) and two minor elements (Fe and Al). These data are presented in Table 4-4. The method employed for analysis of most of these elements was inductively coupled plasma optical emission spectroscopy (ICPOES) which is generally considered to be more accurate than spark source mass spectrometry (SSMS). However, a feed coal sample from test 200 was analyzed for the trace elements boron and beryllium by SSMS. Oil beryllium was also analyzed by SSMS on a sample from test 203. Mercury was analyzed using cold vapor analysis on samples from tests 200 (coal) and 203 (oil). Several of the oil trace elements were below the ICPOES detection limit. Approximate values were calculated for these elements by using the concentrations found at the scrubber inlet, assuming that essentially all of the oil trace elements reach the scrubber. As no bottom ash was generated during oil firing, this assumption should be valid. The value for oil arsenic presented in the table, 2 ppm, was also calculated because the value obtained from ICPOES analysis, 45 ppm, appeared to be unreasonable compared to both the SSMS value (0.1 ppm) and the typical ranges found in the literature.

TABLE 4-3. SUMMARY OF ULTIMATE FUEL ANALYSES (5 TEST AVERAGES)

Component	Coal		Oil	
	Weight %	σ[†]	Weight %	σ[†]
Moisture	7.15	0.86	~0	-
Carbon	72.10	1.07	86.28	0.39
Hydrogen	4.28	0.06	10.92	0.03
Nitrogen	0.92	0.07	0.36	0.06
Chlorine	0.12	0.02	N.A.[x]	-
Sulfur	1.64	0.23	1.96	0.08
Ash	9.90	0.85	0.02	0.004
Oxygen	3.89	0.23	0.46	0.40
kJ/kg	29,485	459	40,741‡	-

[†] σ = one standard deviation.

[x] N.A. = not analyzed.

*The heat content of the oil burned is nearly constant at this value; individual values were not available.

TABLE 4-4. CONCENTRATION OF MAJOR TRACE ELEMENTS IN OIL AND COAL

Element	ppm in Fuel Oil*	Typical RangeΔ	Reference	ppm in Coal†	Typical Range††	Reference
Ca	5.50	No data		770	0-1600	3,5
Mg	<0.04	No data		350	0-959	3,5
Sb	0.03**	0.002-0.8	2	85	0.2-8.9	3
As	2.0ΔΔ	0.0006-1.1	2	137	0.5-93	2,3
B	<0.15	No data		2.4 ‡	4-115	2,4
Cd	<3.5	No data		3.5	0.1-65	3
Cr	2.2	0.002-0.02	2	48	4-144	2,4
Co	<1.25	No data		127	0.5-43	2,3
Cu	1.40	No data		72	3-61	2,3
Fe	12.3	0.003-14	2,6	12,250	0.3-40,000	3,5
Pb	2.6**	No data		85	4-218	2,3
Mn	0.4**	0.001-6	2	12	6-181	3
Mo	2.9**	<0.1-1.5	2	293	0.4-30	2,3
Ni	16.0	14-68	7	37	2-80	2,3
V	36.5	15-590	7	47	2-147	2,3,4
Zn	3.0	No data		56	6-5,350	3
Se	0.7**	0.03-1	2	73	0.4-74	3,4
Sr	0.23	No data		68	No data	
Al	3.5	No data		14,000	0.4-40,700	3,5
Zr	<0.05	No data		270	8-133	3
Be	<0.05x	No data		2.3 ‡	0.6-4.1	2
Hg	0.09xx	0.02-30	2	0.14Y	0.07-0.49	2

* Test 202-4.

Δ Except for V and Ni, these ranges are for U.S. and foreign crude oils. Ranges of V and Ni concentrations are for fuel oils.

† Average of two feed coal samples from test 201-1.

†† Typical range for Appalachian and Eastern Interior Basin coals.

** Values were calculated from concentrations at the scrubber inlet when ICPOES analysis provided upper limit data only.

ΔΔ Arsenic concentration calculated from concentration at the scrubber inlet (see text).

x Performed by SSMS on a feed oil sample from test 203.

‡ Performed by SSMS on a feed coal sample from test 200.

xx Performed by cold vapor analysis on a feed oil sample from test 203.

Y Performed by cold vapor analysis on a fuel coal sample from test 200.

Considering the uniformity of fuel ultimate analyses obtained during the test periods, it appears reasonable to assume that tabulated trace and minor element analyses are typical of the fuels fired during the five day test period. Although analyses of other coal samples from the same source (mine or cleaning plant) are not available for direct comparison, analyses of most trace and minor elements presented in Table 4-4 appear to be consistent with concentration limits typifying Appalachian and Eastern Interior Basin coals. No coal strontium analyses were found for comparison. Trace elements present in somewhat higher concentrations than are indicated to be typical by the limited published data are antimony, arsenic, cobalt, copper, molybdenum, and zirconium. Typical ranges of some trace and minor elements in U.S. and foreign crude oils and for nickel and vanadium in fuel oils are also presented in Table 4-4 for comparison. Analyses of most trace and minor elements for which typical oil values are available appear to be consistent with the literature values. Arsenic and molybdenum values are on the high side, and chromium is quite a bit higher than the typical crude oil values However, the significance of these higher concentrations is not apparent due to the limited quantity of published data and the complete absence of source specific data.

STACK EMISSIONS

As discussed previously, the wet scrubber unit processed a slipstream of the total flue gas generated by the furnace. Analyses of the slipstream have been used to estimate total boiler emissions on the basis of 100% of the flue gas being processed by the scrubber. That is, it was assumed that additional scrubber modules could be added to the system such that the total flue gas output would be processed with a mean scrubber efficiency identical to that obtained using the pilot scrubber. All emissions data presented in the following sections are based on this assumption.

Criteria Pollutants

Federal New Source Performance Standards (NSPS) currently in effect define allowable emission rates of NO_x (as NO_2), SO_2 and total particulates from fossil fuel fired utility boilers having 25 MW output or greater. More stringent limitations have been proposed by EPA for NO_x and total particulate emissions and additional limitations on SO_2 emissions are being considered for proposal. Federal NSPS do not currently address either CO or total hydrocarbon emissions. Existing NSPS and corresponding proposed or potential emission standards for coal and oil-fired utility boilers are summarized in Table 4-5.

Similar standards relating to industrial units have not been promulgated to date. Therefore, criteria pollutant emission data presented in this section will be discussed in the context of existing and proposed Federal NSPS for utility boilers.

As mentioned previously, 5 tests were performed on the Firestone industrial boiler for each fuel. Criteria pollutant concentrations were generally measured at frequent intervals during each test and averaged to obtain the mean concentrations for each test. The 5-test averages of criteria pollutant emissions data are presented in Table 4-6. Average emissions data from the individual tests are presented in Tables 4-7 and 4-8 for coal and oil, respectively. Additionally, the 5-test averages of scrubber inlet data are presented in Table 4-9 for comparison with the EPA AP-42 (Reference 8) emission factors for uncontrolled sources. Tabulated AP-42 emission factors are for 10 MW industrial boilers firing the appropriate fuel. Factors for coal-fired boilers are specific to dry bottom units. The data are discussed by specific compound in the ensuing sub-sections.

Nitrogen Oxide

Mean NO_x emission factors prior to FGD processing were 421 ng/J (0.98 lb/MM Btu) and 168 ng/J (0.39 lb/MM Btu) for coal and oil, respectively. The full load NO_x emission factors prior to FGD processing were 491 ng/J (1.14 lb/MM Btu) for coal firing and 175 ng/J (0.41 lb/MM Btu) for oil firing. The full load emission factor for coal firing is nearly 43% higher than the average emission factor of 343 ng/J (0.80 lb/MM Btu) tabulated in AP-42. On the other hand, the emission factor for oil firing is 19% lower than the tabulated AP-42 emission factor of 217 ng/J (0.51 lb/MM Btu). However, examination of published data from industrial boilers indicates that each emission factor is well within the range typical for the respective fuel (Reference 9). Average measured NO_x emission factors

TABLE 4-5. EXISTING AND PROPOSED FEDERAL EMISSION STANDARDS

Compound	Coal-Fired Utilities		Oil-Fired Utilities	
	NSPS	Proposed or Potential Standard	NSPS	Proposed or Potential Standard
NO_x (as NO_2)	300 ng/J (0.7 lb/MM Btu)	220 ng/J (0.50 lb/MM Btu) max. with 65% reduction.	129 ng/J (0.30 lb/MM Btu)	129 ng/J (0.30 lb/MM Btu) max. with 65% reduction
SO_2	520 ng/J (1.2 lb/MM Btu)	520 ng/J (1.2 lb/MM Btu) max. with 90%* reduction to 85 ng/J (0.20 lb/MM Btu)	344 ng/J (0.80 lb/MM Btu)	344 ng/J (0.80 lb/MM Btu) max. with 90%* reduction to 85 ng/J (0.20 lb/MM Btu)
Total Particulates	43 ng/J (0.10 lb/MM Btu)	13 ng/J (0.03 lb/MM Btu) max. with 99% reduction	43 ng/J (0.10 lb/MM Btu)	13 ng/J (0.03 lb/MM Btu)

*The 90% reduction is a potential standard.

TABLE 4-6. CRITERIA POLLUTANT EMISSIONS FOR AN INDUSTRIAL BOILER IN THERMAL UNITS

Pollutant	ng/J (lb/MM Btu)			
	Coal Firing		Oil Firing	
	Before Scrubber	After Scrubber	Before Scrubber	After Scrubber
NO_x (as NO_2)	421 (0.98)	372 (0.87)	168 (0.39)	161 (0.37)
CO	15.9 (0.04)	14.3 (0.03)	5.47 (0.01)	5.31 (0.01)
SO_2	1112 (2.59)	36.3 (0.08)	993 (2.31)	26.8 (0.06)
Organics (as CH_4)	5.79 (0.01)	6.29 (0.01)	2.49 (0.01)	2.74 (0.01)
Total Particulates	2951 (6.86)	18.6 (0.04)	113 (0.26)	17.6 (0.04)

TABLE 4-7. SUMMARY OF CRITERIA POLLUTANT EMISSIONS - COAL FIRING

Test No.	ng/J (lb/MM Btu)							
	NO_x (as NO_2)	CO	SO_2	HC (as CH_4)	C_1 - C_6 Organics	C_7 - C_{16} Organics	Organics Higher Than C_{16}	Total Particulates
200 Inlet	417 (0.97)	20.7 (0.05)	1009 (2.35)	3.79 (0.01)	<5.49 (<0.01)	0.34 (0.00)	2.28 (0.01)	2361 (5.49)
200 Outlet	367 (0.85)	18.5 (0.04)	25.4 (0.06)	4.22 (0.01)	<5.49 (<0.01)	0.27 (0.00)	0.33 (0.00)	14.3 (0.03)
201-1 Inlet	491 (1.14)	16.5 (0.04)	1284 (2.99)	4.35 (0.01)	<5.65 (<0.01)	--	--	3122 (7.26)
201-1 Outlet	457 (1.06)	15.7 (0.04)	39.0 (0.09)	5.22 (0.01)	<5.65 (<0.01)	--	--	20.9 (0.05)
201-2 Inlet	455 (1.06)	17.7 (0.04)	1295 (3.01)	0.88 (0.00)	<5.75 (<0.01)	--	--	--
201-2 Outlet	358 (8.33)	15.9 (0.04)	35.5 (0.08)	1.33 (0.00)	<5.75 (<0.01)	--	--	--
201-3 Inlet	330 (0.77)	16.2 (0.04)	1028 (2.39)	10.9 (0.03)	<5.69 (<0.01)	--	--	--
201-3 Outlet	258 (0.60)	12.7 (0.03)	31.8 (0.07)	10.9 (0.03)	<5.69 (<0.01)	--	--	--
201-4 Inlet	409 (0.95)	8.56 (0.02)	942 (2.19)	8.95 (0.02)	<5.06 (<0.01)	--	--	3370 (7.84)
201-4 Outlet	420 (0.98)	8.95 (0.02)	49.7 (0.12)	9.73 (0.02)	<5.06 (<0.01)	--	--	20.6 (0.05)
Average Inlet	421 (0.98)	15.9 (0.04)	1112 (2.59)	5.79 (0.01)	<5.53 (<0.01)	0.34 (0.00)	2.28 (0.01)	2951 (6.86)
Average Outlet	372 (0.87)	14.3 (0.03)	36.3 (0.08)	6.29 (0.01)	<5.53 (<0.01)	0.27 (0.00)	0.33 (0.00)	18.6 (0.04)

TABLE 4-8. SUMMARY OF CRITERIA POLLUTANT EMISSIONS - OIL FIRING

Test No.	ng/J (lb/MM Btu)							
	NO_x	CO	SO_2	$HC^†$ (as CH_4)	$C_1 - C_6$ Organics	$C_7 - C_{16}$ Organics	Organics Higher Than C_{16}	Total Particulates
202-1 Inlet	175 (0.41)	5.08 (0.01)	938 (2.18)	2.84 (0.01)	<4.63 (< 0.01)	--	--	166 (0.39)
202-1 Outlet	166 (0.39)	4.70 (0.01)	32.1 (0.07)	3.20 (0.01)	<4.63 (< 0.01)	--	--	20.2 (0.05)
202-2 Inlet	175 (0.41)	5.30 (0.01)	1075 (2.50)	4.61 (0.01)	<4.79 (< 0.01)	--	--	--
202-2 Outlet	165 (0.38)	5.03 (0.01)	29.2 (0.07)	5.01 (0.01)	<4.79 (< 0.01)	--	--	--
202-3 Inlet	181 (0.42)	6.22 (0.01)	1085 (2.52)	1.71 (0.00)	<4.73 (< 0.01)	--	--	--
202-3 Outlet	177 (0.41)	5.92 (0.01)	26.7 (0.06)	1.98 (0.01)	<4.73 (< 0.01)	--	--	--
202-4 Inlet	141 (0.33)	5.30 (0.01)	874 (2.03)	0.82 (0.00)	<4.14 (< 0.01)	--	--	59.0 (0.14)
202-4 Outlet	138 (0.32)	5.60 (0.01)	19.2 (0.04)	0.76 (0.00)	<4.14 (< 0.01)	--	--	15.0 (0.03)
203 Inlet*	--	--	--	--	--	0.17 (0.00)	2.61 (0.01)	--
203 Outlet*	--	--	--	--	--	0.02 (0.00)	0.43 (0.00)	--
Average Inlet	168 (0.39)	5.47 (0.01)	993 (2.31)	2.49 (0.01)	<4.57 (< 0.01)	0.17 (0.00)	2.61 (0.01)	113 (0.26)
Average Outlet	161 (0.37)	5.31 (0.01)	26.8 (0.06)	2.74 (0.01)	<4.57 (< 0.01)	0.02 (0.00)	0.43 (0.00)	17.6 (0.04)

*Emission factors were computed assuming an O_2 concentration of 5.5%, the average concentration for test 202.

†Total hydrocarbons as determined by FID.

TABLE 4-9. COMPARISON OF CRITERIA POLLUTANT EMISSIONS WITH EMISSION FACTORS FOR UNCONTROLLED BOILERS

Pollutant	ng/J (lb/MM Btu)			
	Coal Firing		Oil Firing	
	Test Data Before Scrubber	AP-42 Emission Factor*	Test Data Before Scrubber	AP-42 Emission Factor*
NO_x (as NO_2 at full load)	491 (1.14)	343 (0.80)	175 (0.41)	217 (0.51)
CO	15.9 (0.04)	19 (0.04)	5.47 (0.01)	14.7 (0.03)
SO_2	1112 (2.59)	1189 (2.77)	993 (2.31)	904 (2.10)
Organics (as CH_4)	5.79 (0.01)	5.72 (0.01)	2.49 (0.01)	2.94 (0.01)
Total Particulates	2951 (6.86)	3212 (7.47)	113 (0.26)	29.4 (0.07)

*Factors are computed from AP-42 values for uncontrolled sources using the national average heating values of 11,263 Btu/lb for bituminous coal and 146,285 Btu/gal for fuel oil,[10].

after FGD were 372 ng/J (0.87 lb/MM Btu) for coal firing and 161 ng/J (0.37 lb/MM Btu) for oil firing. As such, controlled NO_x emission rates exceed NSPS limitations by 23 to 25% (NSPS for NO_x is 300 ng/J for coal and 129 ng/J for oil). Data presented in Tables 4-1, 4-7 and 4-8 indicate that NO_x emission varied with boiler load for both fuels, as expected. NO_x emission factors measured at the scrubber inlet are presented in Figure 4-1 as a function of boiler loading for both fuels. The straight line plots presented in the figure were determined by linear regression analyses of the data. It is interesting to note that these lines have very similar slopes, 6.72 ng/J·% loading for coal firing and 4.79 ng/J·% loading for oil firing. These data indicate that for boiler loadings between 90 and 100%, NO_x emission factors from coal firing are approximately three times greater than from oil firing. While this factor of three compares favorably with the ratio of fuel nitrogen contents (312 ng N/J in coal and 88.4 ng N/J in oil leads to a fuel nitrogen ratio of 3.5), total NO_x emissions are composed of both thermal and fuel NO_x components. Laboratory data indicate that for these fuel nitrogen concentrations, 30 to 60% of the fuel nitrogen might be expected to form NO_x, [1]. Therefore, fuel nitrogen content may be a principal factor in the difference between NO_x emissions from coal and oil-fired units.

NO_x data generally indicate a reduction of NO_x emissions across the scrubber for both fuels; the magnitude of this apparent reduction ranges from approximately zero to 24% for coal firing and from 2 to 6% for oil firing. However, NO_x reductions measured during coal firing could not be correlated to variables monitored during testing (NO_x concentration, flue gas temperature, flow rates). Further, NO_x reduction trends paralleled trends in CO reduction which suggested a sampling phenomenon rather than chemical removal. Subsequent examination of the sampling train during oil firing tests revealed a small air leak in the sampling line to the scrubber outlet. This problem, associated with a faulty coupling, was rectified prior to tests 202-3 and 202-4. Data from these latter tests indicate NO_x removals of approximately 2% across the scrubber. Higher removals obtained earlier during the test period are considered to be reflective, at least in part, of air leak problems and must be held suspect. NO_x removal in both wet and dry FGD systems has been reported in the

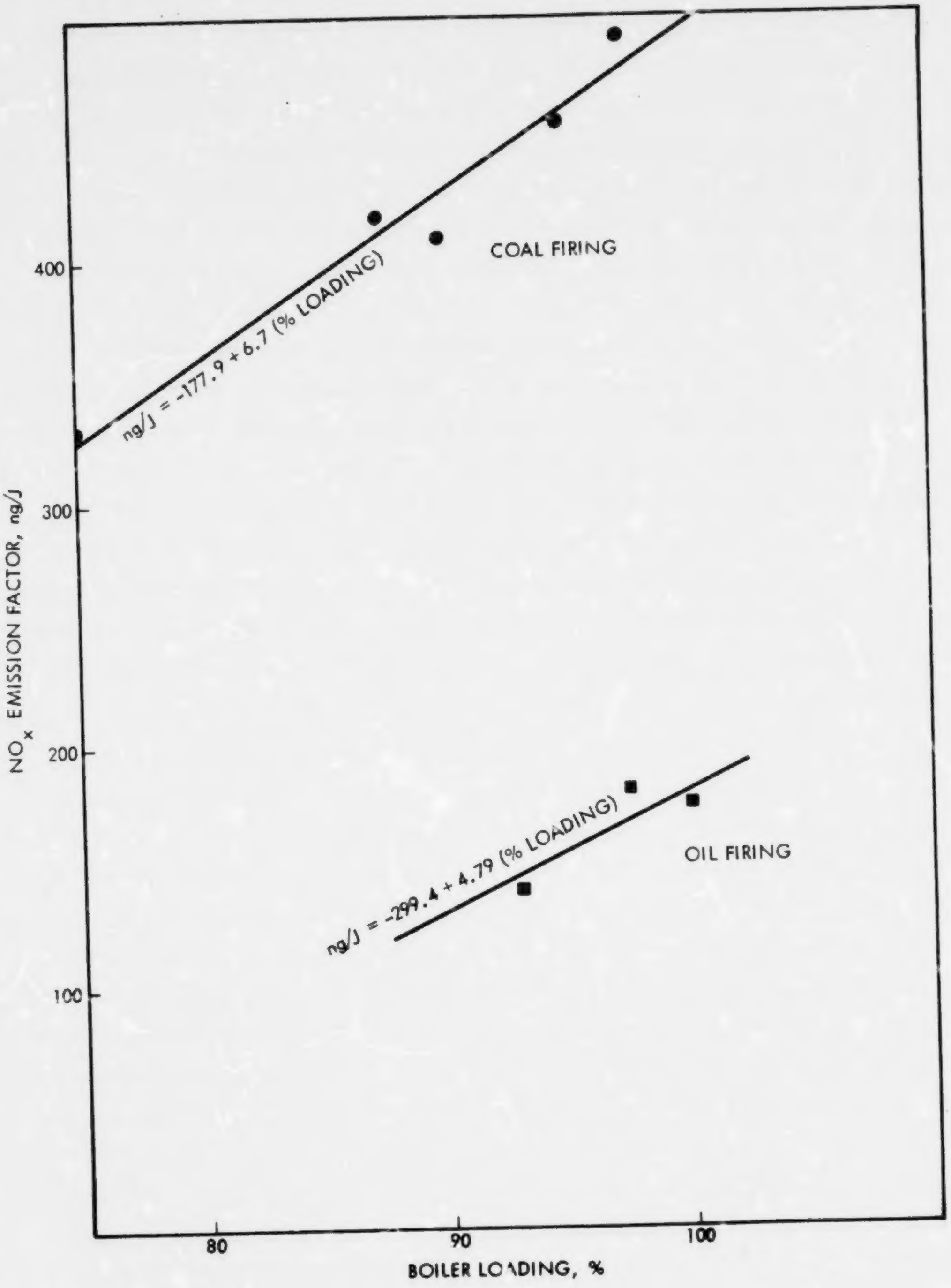

Figure 4-1. The Effect of Boiler Loading on NO$_x$ Emission Factors

literature, although no information is available regarding the chemistry of such occurences, [11], [12]. It is feasible that some degree of NO_x removal may be effected by dissolution of NO_2 in the slightly acidic scrubber solution.

Carbon Monoxide

Emission rates of CO prior to FGD were 15.9 ng/J (0.04 lb/MM Btu) and 5.47 ng/J (0.01 lb/MM Btu) for coal and oil firing, respectively. Average measured CO emissions for coal firing compare well with the AP-42 emission factor of 19 ng/J (0.04 lb/MM Btu). However, CO emissions for oil firing are 63% lower than the respective AP-42 value of 14.7 ng/J (0.03 lb/MM Btu). Thus, while AP-42 data indicate oil firing CO emission factors to be 23% lower than those for coal firing, measured data for coal and oil firing differ by a factor of three. A slight reduction of CO emissions across the scrubber was observed during most tests. Average CO reductions for coal and oil firing were 10 and 3% respectively. As discussed previously, CO reduction trends during coal firing and early oil firing tests are reflective, to some extent, of air leaks in the flue gas sampling train. Further, at these low CO concentrations, analytical sensitivity is in the range of 7-15% of the measured value. Therefore, the slight reductions are considered to be of little significance.

Sulfur Dioxide

Average SO_2 emission rates prior to scrubbing were 1112 ng/J (2.59 lb/MM Btu) and 993 ng/J (2.31 lb/MM Btu) for coal and oil firing, respectively. These uncontrolled emission factors correspond well with the respective AP-42 values of 1189 ng/J (2.77 lb/MM Btu) for coal firing and 904 ng/J (2.10 lb/MM Btu) for oil firing. Average SO_2 emission rates after scrubbing were 36.3 ng/J (0.08 lb/MM Btu) for coal firing and 26.8 ng/J (0.06 lb/MM Btu) for oil firing. A mean scrubber efficiency of 97% is indicated for both fuels by these data. Measured SO_2 emission rates after scrubbing are lower than either existing or potential NSPS limitations.

Hydrocarbons

Total organic emissions, expressed as methane, were analyzed with a Flame Ionization Detector (FID) during coal and oil firing tests. Average hydrocarbon emissions prior to scrubbing were 5.79 ng/J (0.01 lb/MM Btu) for coal firing and 2.49 ng/J (0.01 lb/MM Btu) for oil firing. Measured emissions rates correspond well with the AP-42 values of 5.72 ng/J (0.01 lb/MM Btu) for coal firing and 2.94 ng/J (0.01 lb/MM Btu) for oil firing. It should be noted that, during these tests, the analyzed flue gas slipstream was processed through a gas conditioner situated ahead of the FID in the analytical train. Therefore, higher molecular weight organics may have been condensed or scrubbed from the flue gas prior to analysis.

Hydrocarbon emissions measured by FID appeared, on the average, to increase across the scrubber by approximately 10% for both fuels. These data were evaluated in terms of real time scrubber inlet and outlet data pairs obtained not more than 30 minutes apart. The average increase in hydrocarbons across the scrubber is not statistically significant for coal firing data due to concentration fluctuations during testing. However, real time data pairs measured during coal firing do show a statistically significant difference with scrubber outlet samples being biased high relative to inlet samples. The magnitude of this bias is approximately 5 ppm (1.5 ng/J at the excess oxygen levels measured). The cause of the observed bias is not known at the present time although the possibility of moisture interference, improper FID calibration or variable sample gas flow rate has been evaluated and subsequently discarded. Real time data pairs measured during oil firing indicate that hydrocarbon emissions at the scrubber inlet and outlet are not statistically different. Whether the absence of significant bias for oil firing results from the lower emission factor associated with oil firing or reflects differences in combustion products from the two fuels cannot be determined from available data.

In addition to FID analyses of total hydrocarbons, gas chromatograph analyses were performed on limited bag samples of flue gas and catches from the Level 1 sampling (SASS train). Additionally, gravimetric analyses were performed on Level 1 samples to quantify high molecular weight organics. Each bag sample was collected over an interval of 30 to 45 minutes, with a single sample being collected per test. These samples were utilized to measure C_1 to C_6 hydrocarbons. The SASS train collects approximately 30 cubic meters of flue gas which are drawn isokinetically during the test. Samples from the SASS train were analyzed to determine organics higher than C_6. The C_7 to C_{16} fraction was determined by gas chromatograph while organics higher than C_{16} were determined gravimetrically.

Analytical results for scrubber outlet SASS train XAD-2 resin samples were not available due to sample handling problems. However, data from coal- and oil-fired utility boilers were utilized to obtain an average ratio of resin-absorbed organics to all other organics collected by the SASS train for each fuel. These ratios were used in conjunction with data from the scrubber outlet probe rinse, resin module rinse, particulate organics and other organic catches from the SASS train to estimate the resin catch. Calculated outlet organic data from the C_7 to C_{16} and higher than C_{16} organic fractions are considered to be accurate to within a factor of three to four.

Emissions of hydrocarbons higher than C_{16} and scrubber removal efficiencies for this fraction appear to be similar for coal and oil firing tests. As indicated in Tables 4-7 and 4-8, emission factors for organics higher than C_{16} for coal and oil firing differ by less than 15% with 2.28 ng/J (0.01 lb/MM Btu) for coal firing and 2.61 ng/J (0.01 lb/MM Btu) for oil firing prior to scrubbing. Organics higher than C_{16} comprise 28 to 60% of the scrubber inlet hydrocarbons during coal firing and 35 to 94% during oil firing. Emissions of organics higher than C_{16} were reduced to 0.33 ng/J (85% removal) and 0.43 ng/J (83% removal) for coal and oil firing, respectively.

Emissions of C_7 to C_{16} fractions prior to scrubbing were 0.34 ng/J for coal firing and 0.17 ng/J for oil firing. These emission rates indicate that the C_7 to C_{16} fraction represents less than 9% of the total organic emissions prior to scrubbing during coal firing and less than 6% during oil firing. Emissions of the C_7 to C_{16} fraction after scrubbing were 0.27 ng/J and 0.02 ng/J for coal and oil firing, respectively. These data appear to indicate that removal of the C_7 to C_{16} fraction by scrubbing was 20% for coal firing and 88% for oil firing. However, noting the uncertainty in outlet organic levels described previously, the 20% removal observed for coal firing may actually be as high as 97% while the 88% removal for oil firing may be as low as 53%. Hence, while it appears that some removal of C_7 to C_{16} fraction was achieved for both fuels, definite conclusions regarding the relative removals for each fuel cannot be drawn.

Chromatographic analyses performed on the C_1 to C_6 hydrocarbon fractions did not indicate the presence of these organics at the detection limits indicated in Tables 4-7 and 4-8, namely 5.53 ng/J for coal and 4.57 ng/J for oil. However, note that the emissions of C_7 and higher organics prior to scrubbing are essentially the same for coal and oil firing and that removal of these organics by scrubbing is between 2.02 ng/J and 2.33 ng/J. Further, FID data do not show a decrease in organics across the scrubber. These observations appear to indicate that the flue gas slipstream analyzed by FID contained light hydrocarbon fractions but did not include higher molecular weight organics. This may be attributed to processing the flue gas through a gas conditioner prior to FID analysis. As such, FID data may be reflective of C_1 to C_6 hydrocarbon emissions and indicate that the coal firing produces more C_1 to C_6 hydrocarbons than does oil firing.

Total Particulates

Average emission rates of total particulates prior to scrubbing were 2951 ng/J (6.86 lb/MM Btu) for coal firing and 113 ng/J (0.26 lb/MM Btu) for oil firing. A mass balance of the coal ash indicates that approximately 75% of the total ash was processed by the scrubber and that multiclones located upstream of the scrubber removed little or no particulate. This observation was verified by site operators who noted that the multiclone unit was subject to mechanical failure during both coal and oil firing. Hence, particulate loadings measured at the scrubber inlet appear to be representative of uncontrolled emissions. Mean particulate loadings at the scrubber inlet during coal firing are approximately 8% lower than the value of 3212 ng/J (7.47 lb/MM Btu) presented in AP-42, which represents rather good agreement. On the other hand, the average particulate emission factor for oil firing is nearly a factor of four greater than the tabulated AP-42 value of 29.4 ng/J (0.07 lb/MM Btu). However, data presented in Table 4-8 show that the oil firing particulate loading prior to scrubbing was substantially larger during test 202-1 than during test 202-4, indicating that coal ash from previous testing may have been emitted during early oil firing tests. If particulate data from test 202-4 are assumed to be representative of oil firing emissions, the particulate emission rate of 59 ng/J (0.14 lb/MM Btu) measured at the scrubber inlet exceeds the AP-42 value by a factor of two. This assumption appears to be valid since data from Polarized Light Microscopy analyses (PLM) indicate that particulates from test 202-4 are composed primarily of oil soot and sulfate compounds (refer to the Inorganic subsection for analysis).

Total particulate emissions after scrubbing were 18.6 ng/J (0.04 lb/MM Btu) for coal firing and 17.6 ng/J (0.04 lb/MM Btu) for oil firing. These controlled particulate emission rates correspond to 99% and 84% removal efficiencies for coal and oil firing, respectively. However, based on the oil firing particulate catch known to be free of coal ash contamination, the scrubber efficiency appears to be 75%. Controlled particulate emissions for both coal and oil firing are well below the NSPS limitation of 43 ng/J (0.10 lb/MM Btu) although they are slightly higher than the proposed limitation of 13 ng/J (0.03 lb/MM Btu).

Particulate Size Distribution

Size distributions of particulates at the scrubber inlet and outlet were determined by two methods. Due to the high particulate loading at the scrubber inlet during coal firing, PLM analyses were utilized to obtain a size distribution in terms of optical diameter and number of particles per size range. All other particulate size distribution determinations involved streams with substantially lower solids loadings and, therefore, an Anderson cascade impactor was used. The cascade impactor data differs from PLM analyses in that size distributions are determined in terms of aerodynamic diameter and weight percent in each size range. Thus, data from the two methods cannot be directly compared. For this reason, the PLM data have been converted to the same basis as the impactor data by assuming that particulate density is independent of particle diameter. This is a reasonable assumption because the major components of the particulates generated from coal combustion, the aluminosilicates and iron oxides, are known to partition equally among small and large particulates. With the constant density assumption, the weight distribution in each size range would be proportional to the product of the number distribution and the particulate volume representing the size range. The particulate volume was calculated based on the geometric mean diameter for the size range.

Particulate size distribution data from coal and oil firing tests are summarized in Table 4-10. These data show a significant change in particulate size distribution before and after scrubbing for both fuels. The increase in the fraction of finer particulates across the scrubber indicates that coarse particulates were removed more efficiently than fine particulates for both coal and oil firing tests. This is further indicated by emission rate data presented in Table 4-11 which shows that particulates larger than 3μm were removed with efficiencies of at least 97% while particulates smaller than 3μm showed little or no removal.

As discussed previously, particulates from early oil firing tests collected prior to scrubbing appear to contain residual particulate from coal fired tests. Since coal particulate is generally coarser than oil particulate, contaminated oil particulate would appear to be somewhat coarser than pure oil particulate. Thus, while data in Table 4-10 show that oil particulate is substantially finer than coal particulate, the difference in size distributions is probably not as great as would have been found if a pure oil particulate sample had been sized.

It is also interesting to note that for coal-fired particulates less than 3 μm in size, there is a net increase in emission rates across the scrubber (Table 4-11). This net increase indicates that the venturi scrubber is probably not effective in removing the fine particulates present in the flue gas, and that fine particulates may be generated within the scrubber. Based on the analysis of SO_3 and $SO_4^=$ emission data, it has been estimated that up to 40% of the fine particulate emissions at the scrubber outlet could be contributed by scrubber generated $NaHSO_4$. The remaining portion of the net increase in fine particulates across the scrubber can probably be attributed to the uncertainties associated with the assumptions used in

TABLE 4-10. SCRUBBER INLET AND OUTLET PARTICULATE SIZE DISTRIBUTION

Aerodynamic Diameter Size Range, Microns	Weight %			
	Coal Firing (Test 201-1)		Oil Firing (Test 202-1)	
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet
< 1	0.0017	62	20	83
1 - 3	0.041	30	1	12
3 - 10	2.24	7	74	5
> 10	97.7	1	5	0

TABLE 4-11. EMISSION RATES OF PARTICULATES

Aerodynamic Diameter Size Range, Microns	Coal Firing (Test 201-1)			Oil Firing (Test 202-1)		
	kg/hr		Removal Efficiency	kg/hr		Removal Efficiency
	Scrubber Inlet	Scrubber Outlet		Scrubber Inlet	Scrubber Outlet	
< 1	0.0055	1.30	<0	4.48	2.27	49.2
1 - 3	0.13	0.63	<0	0.22	0.33	<0
3 - 10	7.3	0.15	97.9	16.6	0.14	97.4
> 10	316.5	0.021	>99.9	1.12	0.00	100
Total	324.0	2.10	99.3	22.4	2.74	87.8

converting PLM number size distribution data to weight size distribution, and to calcium sulfite heminydrate ($CaSO_3 \cdot 1/2\ H_2O$) particulates generated by the scrubber.

Although a very slight increase in 1-3μm oil-fired particulates was observed, a net decrease in particulates less than 3μm was observed for oil fired testing. Also, compounds associated with scrubber solution were not conclusively identified in the oil-fired particulates at the scrubber outlet. However, based on the results of coal-fired testing, it appears reasonable that scrubber generated particulates were present in the scrubber outlet stream during oil firing but that the high fine particulate loading associated with oil firing masked detection of these materials.

Sulfur Compounds: SO_2, SO_3, and $SO_4^=$

A pulsed fluorescent analyzer was used to continuously monitor SO_2 emissions for the coal and oil tests. SO_3 was determined as H_2SO_4 using the Goksoyr-Ross controlled condensation system, and $SO_4^=$ was determined by anion analysis of the particulate extracts from the Method 5 sampling train. A summary of these analytical results is presented in Table 4-12. As can be seen from the sulfur balance, 90 to 94% of the input sulfur is emitted as SO_2 when emissions are uncontrolled. The removal efficiency for SO_2 is high: 95 to 97% for coal firing and 97 to 98% for oil firing. About 30% of the SO_3 was also removed by the scrubber. The relatively poor removal efficiency for SO_3 is an indication that SO_3 is either present as very fine aerosols in the scrubber inlet, or is converted to very fine aerosols as the flue gas stream is rapidly cooled inside the scrubber. The higher $SO_4^=$ removal efficiency indicates that $SO_4^=$ is probably associated with larger particulates, which are efficiently scrubbed.

A comparison of the sulfur oxide emissions is best made by comparing emission rates which are normalized to the amount of fuel sulfur available. These are listed in the column "% of fuel sulfur found in flue gas at inlet" in Table 4-12. For SO_2, these values are almost the same for coal and oil. For SO_3, the values for oil were 50 to 75% higher than for coal. This result is generally attributed to the fact that vanadium and nickel, which catalyze the oxidation of SO_2 to SO_3, are usually present in higher concentrations in oil than in coal. For sulfates, the normalized emission

TABLE 4-12. SO_2, SO_3, and $SO_4^=$ EMISSIONS FROM COAL AND OIL FIRING

Pollutant	Oil					Oil				
	Test	Scrubber Inlet ng/J	Scrubber Outlet ng/J	% of Fuel Sulfur Found in Flue Gas at Inlet	Removal Effi- ciency %	Test	Scrubber Inlet ng/J	Scrubber Outlet ng/J	% of Fuel Sulfur Found in Flue Gas at Inlet	Removal Effi- ciency %
SO_2	201-1	1280	37.8	92	97	202-1	940	32.2	92	97
	201-4	937	47.8	94	95	202-4	874	19.2	90	98
SO_3	201-1	7.2	4.9	0.4	33	202-1	7.5	5.3	0.6	29
	201-4	4.9	3.3	0.4	32	202-4	8.4	6.0	0.7	28
$SO_4^=$	201-1	66.3	8.0	3	88	202-4	22.9	9.1	1.6	60
Total	201-1			95		202-4			92	

rate for coal is twice that for oil. Because the SO_3 concentration levels are lower than the $SO_4^=$ levels, this cannot be satisfactorily explained by simply assuming a higher rate of reaction of gaseous SO_3 with ash particulates to form metallic sulfates. A possible mechanism of metallic sulfate production is as follows: the metal oxides in the ash may serve as catalysts for the reaction of SO_2 to SO_3. The SO_3, which is adsorbed on the ash surface, may then react with the surface to form a metallic sulfate, or may desorb and then collide with ash particulates and form the sulfate. It is thus proposed that in the coal-fired case the reaction is catalyzed by metallic ash constituents, and SO_3 is formed as an adsorbed intermediate, which then usually reacts with the ash on which it is adsorbed. In the oil-fired case, mainly gaseous SO_3 is formed, the reaction being catalyzed by Ni and V.

A comparison of scrubber efficiencies shows that for the gaseous sulfur oxides, the removal efficiency does not depend upon the fuel used. However, sulfates are not removed with equal efficiency from flue gases from coal and oil firing. The higher sulfate removal from the coal flue gases is explained by the fact that the particulates from coal firing are larger than those from oil, and the scrubber removes larger particulates more efficiently than smaller particulates.

Table 4-13 shows the breakdown of the sulfate emissions into the water and acid soluble fractions before and after the scrubber. While both types of sulfates were removed by the scrubber, the fraction of water soluble sulfates increased from 56 to 88% during oil firing and from 24 to 97% during coal firing. One explanation is that the acid soluble fraction is more efficiently removed than the water soluble fraction. This cannot be checked by comparing the removal efficiencies of the major element cations (Tables 4-16 and 4-17) as a function of the solubility of their sulfates because the types of sulfates present are not known. A second explanation may be that the water and acid soluble fractions are removed with comparable efficiency, and that the scrubber contributes shall quantities of water soluble sulfate to the gas stream passing through. Because of this possibility, an analysis effort utilizing Fourier Transform Infrared

TABLE 4-13. SUMMARY OF SULFATE EMISSIONS DURING COAL AND OIL FIRING

	Emission Rate, ng/J			
	Coal - Test 201-1		Oil - Test 202-4	
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet
Water Soluble	16.0 (24%)	8.1 (97%)	12.9 (56%)	8.0 (88%)
Acid Soluble	51.2 (76%)	0.2 (3%)	10.0 (44%)	3.5 (12%)
Total	67.2	8.3	22.9	9.1

Analysis (FTIR) and X-Ray Diffraction (XRD) analysis was initiated to determine the nature of $SO_4^=$ emissions. For the dual alkali system, possible sulfate species would be $CaSO_4$ and $Ca(HSO_4)_2$ from the scrubber regeneration step, $NaHSO_4$ and Na_2SO_4 from oxidation of $NaHSO_3$ and Na_2SO_3. Calcium sulfate and bisulfate are ruled out because of the low calcium concentration at the outlet (see Tables 4-14 and 4-15). In the coal test, FTIR and XRD confirmed the presence of sodium bisulfate at the scrubber outlet, but not at the scrubber inlet. This is positive proof that sulfates are generated within the scrubber and emitted in the scrubber effluent gas in the coal-fired test. Based on these findings, it is believed that $NaHSO_4$ emissions from the scrubber are on the order of 1 ng/J (the difference between total sulfate and H_2SO_4 emissions determined as SO_3). Furthermore, if one assumes that only a small fraction of the H_2SO_4 was collected on the filter because of the high filter temperature, then the measured sulfate emissions could be almost totally metallic sulfates, indicating that the scrubber contribution could be as high as 8 ng/J. This amount of scrubber generated $NaHSO_4$ could account for 40% of the fine particulate (<3 μm) emissions at the scrubber outlet.

In the oil-fired test, FTIR confirmed the presence of $NaHSO_4$ at both the inlet and outlet of the scrubber, but XRD results indicated that $NaHSO_4$ made up less than 1% of the particulate matter in the gas stream

TABLE 4-14. EMISSION CONCENTRATIONS OF TRACE ELEMENTS DURING COAL FIRING - TEST 201-1

Trace Element	Scrubber Inlet mg/m^3	Scrubber Outlet mg/m^3	MATE Value mg/m^3	Degree of Hazard[‡] Scrubber Inlet	Degree of Hazard[‡] Scrubber Outlet
Be[*]	0.1	0.002	0.002	50	1.0
Hg[†]	0.011	0.005	0.05	0.22	0.10
Ca	74	0.036	16	4.6	0.002
Mg	19	0.011	6.0	3.2	0.002
Sb	3.7	0.025	0.050	74	0.5
As	7.8	0.22	0.002	3900	110
B[*]	0.2	0.03	3.1	0.07	0.01
Cd	0.47	0.0010	0.010	47	0.1
Cr	2.6	0.13	0.001	2600	130
Co	3.6	0.012	0.050	72	0.24
Cu	9.6	0.020	0.20	48	0.10
Fe	450	2.4	1.0	450	2.4
Pb	8.5	0.021	0.15	57	0.14
Mn	0.78	0.015	5.0	0.16	0.003
Mo	10	0.027	5.0	2.0	0.005
Ni	1.4	0.063	0.015	93	4.2
V	3.1	0.058	0.50	6.2	0.12
Zn	2.3	0.048	4.0	0.58	0.012
Se	3.2	0.099	0.200	16	0.50
Sr	11	0.058	3.1	3.5	0.019
Al	480	2.6	5.2	92	0.5
Zr	1.6	0.018	5.0	0.32	0.004
Total	1100	6.2			

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[*] Approximate values as determined by Spark Source Mass Spectrometry (SSMS). The other values presented are determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) analysis.

[†] Mercury was determined by cold vapor analysis of SASS train.

[‡] Degree of hazard is defined as the ratio of the discharge concentration to the MATE value.

TABLE 4-15. EMISSION CONCENTRATIONS OF TRACE ELEMENTS DURING OIL FIRING - TEST 202-4

Element	Scrubber Inlet mg/m^3	Scrubber Outlet mg/m^3	MATE Value mg/m^3	Degree of Hazard	
				Scrubber Inlet	Scrubber Outlet
Be[*]	<0.001	0.001	0.002	<0.50	0.50
Hg[†]	0.0016	0.0002	0.05	0.032	0.004
Ca	0.41	0.070	16	0.026	0.004
Mg	0.31	0.030	6.0	0.052	0.005
Sb	0.062	0.006	0.050	1.24	0.120
As	0.15	0.030	0.002	75.0	15.0
B	0.53	0.039	3.1	0.171	0.013
Cd	0.28	0.066	0.010	28.0	6.60
Cr	0.17	0.018	0.001	170	18.0
Co	0.10	0.012	0.050	2.0	0.24
Cu	0.54	0.007	0.20	2.70	0.035
Fe	4.8	0.28	1.0	4.8	0.28
Pb	0.20	0.013	0.15	1.333	0.087
Mn	0.03	0.004	5.0	0.006	0.001
Mo	0.22	0.025	5.0	0.044	0.005
Ni	1.1	0.20	0.015	73.3	13.33
V	2.7	0.82	0.50	5.40	1.640
Zn	0.61	0.065	4.0	0.153	0.016
Se	0.050	0.006	0.200	0.25	0.03
Sr	0.043	0.001	3.1	0.014	0.0003
Al	5.7	0.48	5.2	1.096	0.092
Zr	0.015	0.001	5.0	0.003	0.0002
Total	18	2.5			

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[*] Beryllium was determined by Spark Source Mass Spectrometry (SSMS). The other values, with the exception of mercury, are determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) analysis.

[†] Mercury was determined by cold vapor analysis of SASS train samples taken during test 203.

whereas sulfates accounted for 40% of the particulate matter at the inlet and 60% at the outlet. It is possible that scrubber generated Na_2SO_4 was added to the scrubber effluent gas, but this has not been confirmed. It would be expected that generation of sulfates by the scrubber would be independent of the type of fuel, other operating conditions being the same. It is not presently known why these results differed in the coal- and oil-fired tests.

Inorganics

Concentrations of 22 major trace elements present in the flue gas during coal and oil firing are presented in Tables 4-14 and 4-15. To assess the hazard potential of these emissions, the emission concentrations are compared with the Minimum Acute Toxicity Effluent (MATE) values. The MATE values are emission level goals developed under direction of EPA, and can be considered as concentrations of pollutants in undiluted emission streams that will not adversely affect those persons or ecological systems exposed for short periods of time, [13]. Tabulated MATE values represent air concentrations which were derived from human health considerations. Analysis of the flue gas generated during coal firing indicates that 18 elements exceeded their respective MATE values at the scrubber inlet and 4 exceeded their MATE values at the scrubber outlet. These four elements which pose a potential hazard are arsenic, chromium, iron and nickel. During oil firing, 11 elements exceeded their respective MATE values at the scrubber inlet and 5 exceeded their MATE values at the scrubber outlet. The 5 elements exceeding their MATE values at the scrubber outlet are arsenic, cadmium, chromium, nickel and vanadium. Elements exceeding their MATE values at the scrubber outlet and which are common to both coal and oil firing are arsenic, chromium and nickel.

The MATE value for arsenic is extremely low because arsenic is a cumulative poison producing chronic effects in humans. MATE values for nickel and chromium are extremely low due to considerations for potential human carcinogenicity. Similarly, the low MATE value for cadmium results from considerations of potential carcinogenic, oncogenic and teratogenic effects upon humans. The MATE value for vanadium is comparatively higher since vanadium has been associated with eye and bronchial irritation without indication of chronic effects. Emissions of arsenic and chromium after scrubbing are below their TLV's which are each 0.5 mg/m^3. And, for coal firing, emissions of nickel after scrubbing are below the TLV value of 0.1 mg/m^3. Hence, if TLV's were used as the basis for comparison, emissions of arsenic, chromium and nickel would be considered less hazardous. For oil firing, emissions of cadmium, nickel and vanadium after scrubbing exceed their TLV values of 0.05, 0.1 and 0.5 mg/m^3, respectively, in addition to exceeding their respective MATE values.

Beryllium emissions after scrubbing were 0.002 mg/m^3 for coal firing and 0.001 mg/m^3 for oil firing. These concentrations may be compared to the beryllium MATE value of 0.002 mg/m^3. At these emission concentrations, the National Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would only be exceeded by boilers of 50 MW capacity or greater for coal firing and 100 MW capacity or greater for oil firing.

Emission factors and mass emission rates for the 22 trace elements analyzed are presented in Tables 4-16 and 4-17. Also presented in these tables are scrubber removal efficiencies for each element. An overall removal efficiency of 99% was obtained for coal firing and 87% was obtained for oil firing. However, some elements were removed with less than the average removal efficiency for their respective fuel. It is interesting to note that, with the exception of iron, all elements which exceeded their MATE values at the scrubber outlet during coal firing were removed with lower than average efficiency. With the exception of chromium, the same observation may be made regarding oil-fired data.

Enrichment factors across the scrubber have been computed for each element and are presented in the last columns of Tables 4-16 and 4-17. The enrichment factor is defined as the ratio of the concentrations of trace elements to aluminum at the scrubber outlet divided by the corresponding ratio at the scrubber inlet. Aluminum is selected as a reference material because it is known to partition equally among particulates of

TABLE 4-16. EMISSION FACTORS AND MASS EMISSION RATES OF TRACE ELEMENTS DURING COAL FIRING - TEST 201-1

Trace Element	Emission Factor, ng/J Scrubber Inlet	Emission Factor, ng/J Scrubber Outlet	Emission Rate, g/hr Scrubber Inlet	Emission Rate, g/hr Scrubber Outlet	Removal fficiency %	Enrichment Factor
Be*	0.04	0.001	5	0.09	98	3.7
Hg†	0.08	0.037	0.50	0.23	55	84
Ca	32	0.015	3300	1.6	99	0.09
Mg	8.2	0.0046	860	0.48	99	0.11
Sb	1.6	0.010	170	1.1	99	1.2
As	3.4	0.092	350	9.7	97	5.3
B*	0.1	0.01	10	1.2	88	2.1
Cd	0.20	0.00042	21	0.044	99	0.4
Cr	1.1	0.054	120	5.7	95	9.5
Co	1.6	0.0050	160	0.53	99	0.6
Cu	4.1	0.0084	430	0.88	99	0.4
Fe	190	1.0	20,000	110	99	0.99
Pb	3.7	0.0088	380	0.92	99	0.5
Mn	0.34	0.0063	35	0.68	98	3.4
Mo	4.3	0.026	450	1.2	99	0.5
Ni	0.60	0.026	61	2.8	95	8.6
V	1.3	0.024	140	2.5	98	3.6
Zn	0.99	0.020	100	2.1	98	3.9
Se	1.4	0.041	140	4.3	97	5.8
Sr	4.7	0.024	500	2.5	99	0.9
Al	210	1.1	22,000	110	99	1.0
Zr	0.69	0.0075	72	0.79	99	2.1
Total	470	2.6	50,000	270	99	

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[*] Appropriate values as determined by SSMS. The other values, with the exception of mercury, were determined by ICPOES analysis.

[†] Mercury was determined by cold vapor analysis of SASS train samples taken during test 200.

TABLE 4-17. EMISSION FACTORS AND MASS EMISSION RATES OF TRACE ELEMENTS DURING OIL FIRING - TEST 202-4

Element	Emission Factor, ng/J		Emission Rate, gm/hr		Removal Efficiency %	Enrichment Factor
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet		
Be[*]	<0.0003	0.0003	<0.04	0.04	Unknown	>11.9
Hg[†]	0.0006	0.0001	0.05	0.006	87	1.48
Ca	0.13	0.022	16	2.7	83	2.03
Mg	0.10	0.0094	12	1.1	91	1.15
Sb	0.02	0.0019	2.5	0.23	91	1.15
As	0.049	0.0094	5.9	1.1	81	2.37
B	0.17	0.012	21	1.5	93	0.87
Cd	0.091	0.021	11	2.5	77	2.80
Cr	0.055	0.0057	6.7	0.69	90	1.26
Co	0.033	0.0038	3.9	0.46	89	1.43
Cu	0.18	0.002	21	0.27	99	0.15
Fe	1.6	0.088	190	11	95	0.69
Pb	0.065	0.0041	7.9	0.50	94	0.77
Mn	0.010	0.0013	1.2	0.15	87	1.58
Mo	0.072	0.0079	8.7	0.95	89	1.35
Ni	0.36	0.063	43	7.7	83	2.16
V	0.88	0.26	110	31	71	3.61
Zn	0.20	0.02	24	2.5	90	1.27
Se	0.016	0.002	2.0	0.23	87	1.43
Sr	0.014	0.0003	1.7	0.038	98	0.28
Al	1.9	0.15	220	18	92	1.0
Zr	0.0049	0.0003	0.59	0.038	94	0.79
Total	6.0	0.78	710	96	87	

[*] Beryllium was determined by SSMS. The other elements, except fluorine, were determined by ICPOES.

[†] Mercury was determined by cold vapor analysis of SASS train samples taken during test 203.

different size*. Enrichment factors presented in the tables indicate that beryllium, antimony, arsenic, chromium, manganese, nickel, vanadium, zinc, selenium and mercury are enriched across the scrubber for both fuels. Additionally, boron and zirconium are enriched during coal firing and calcium, magnesium, cadmium, cobalt and molybdenum are enriched during oil firing.

Trace element enrichment is principally due to the partitioning of trace elements as a function of particulate size, and the greater collection efficiency of the scrubber for large size particulates.

To better characterize combustion generated solids in terms of trace element distribution, the Electron Spectroscopy for Chemical Analysis (ESCA) technique was used to determine surface and subsurface concentrations of elements in the particulates. ESCA results for particulates from both fuels are presented in Tables 4-18 and 4-19 as normalized atom percentages for each particulate catch and penetration. Scrubber inlet data indicate that coarser particulate matter collected by the cyclone differs somewhat from the finer particulates collected on the filter. In the case of coal-fired particulates, the principal difference is the lower silicon content of the coarser particulate. For oil-fired particulate, the principal difference is the higher carbon and lower silicon and oxygen contents of the coarser particulates. It is interesting to note that the filter catch particulates at the scrubber inlet and outlet yielded very similar ESCA analyses at the particle surface and at a 76 Å penetration for oil fired particulates. That this does not hold true for coal-fired particulates may reflect the higher coarse particulate fraction generated and subsequently higher particulate removal efficiency obtained for coal firing. That is, the compositions of coal fired particulates at the scrubber inlet and outlet might be expected to differ more significantly than in the case of oil fired particulates due to the higher coarse particulate loading at the inlet and, consequently, the higher particulate removal efficiency during coal firing.

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* Silicon, iron and scandium have also been used by other investigators as a reference element in the computation of enrichment factors. Notice that iron has no enrichment in this study while silicon and scandium were not measured.

TABLE 4-18. DEPTH PROFILE ANALYSIS OF COAL PARTICULATE WITH CONCENTRATIONS EXPRESSED AS NORMALIZED ATOM PERCENT* - TEST 201-1

		O	Na	S	Si	Al	Fe	Cl	P	V	Ca	C	K
Inlet	Level II cyclone catch	57	4	11	6	7	2	2	1				
	Level II filter catch	56	2.4	11.5	14.1	8	1.4	1.5	1.2		2		
	Level II filter catch; 76 Å	54.2	2.1	4.0	17.9	12.6	2.1	1.3	2.2	1.0	2.7		
Outlet	Level II filter catch	45.7	5.5	13.2	7.1	2.2		1.2	1.1	0.7	1.3	14.9	7.1
	Level II filter catch; 75 Å	48	7.4	11.5	9.0	5.2	1.2	1.1	1.1		1.1	12.1	1.8
	Level II filter catch; 150 Å	48.3	9.1	10.0	10.1	7.7	1.2	1.2	1.2			10.0	1.2
	Level II filter catch; 300 Å	48.3	8.8	6.0	10.6	9.6	2.1	1.0	1.2	0.5		8.0	1.8
	Level II filter catch; 500 Å	47.9	7.3	6.7	10.8	13	1.7	1.2	1.1		1.2	8.1	1.1
	Level II filter catch; 700 Å	47	7.3	6.1	11.6	11.0	2.3	0.9	1.5	0.5	1.0	8.8	1.6

* The atom percent of the 12 elements presented here adds up to 100 percent. Other elements present in the cyclone and filter catches were not studied in ESCA. Hence, the atom percents in this table are normalized atom percents and not absolute atom percents.

TABLE 4-19. DEPTH PROFILE ANALYSIS OF OIL PARTICULATE WITH CONCENTRATIONS EXPRESSED AS NORMALIZED ATOM PERCENT* - TEST 202-4

	O	Na	S	Si	Al	Fe	Cl	P	V	Ca	C	K
Inlet												
Level II Cyclone Catch	38.5	3.2	12.9	2.6	2.3		1.4	0.6	1.2		37.4	
Level II Filter Catch	48.6	4.2	10.7	11.8	3.1		1.3	1.5	1.7		17.2	
Level II Filter Catch; 76Å	46.3	4.7	6.5	17.1	3.3	0.8	1.4	1.1	3.3	0.9	12.9	1.7
Outlet												
Level II Filter Catch	45.5	5.7	9.7	14.6	3.4	1.3	2.3	1.6	1.7		14.1	
Level II Filter Catch; 76Å	53.5	3.2	6.8	22.0	4.0		1.3	1.0	2.0		6.2	

* The atom percent of the twelve elements presented here adds up to 100 percent. Other elements present in the cyclone and filter catches were not studied in ESCA. Hence, the atom percents in this table are normalized atom percents and not absolute atom percents.

As indicated in Table 4-18, some elements, most notably sulfur and carbon, appear to be enriched at the particle surface and somewhat depleted in the bulk of the particle. The opposite trend is observed for aluminum and silicon which are enriched in the bulk of the particulate. These observations indicate that some degree of surface coating of the particle has occurred. Assuming that the bulk of the particulate is homogeneous with respect to aluminosilicates, the thickness of the surface coating can be most readily estimated by considering the concentration of coating elements relative to the concentration of aluminum or silicon. The relative concentration may be plotted as a function of penetration to enable a graphical estimation of coating thickness. Aluminum was selected as the reference element here rather than silicon because the ESCA analyses were run directly on the filter and the silicon content of the filter would interfere with interpretation of the data.

Depth profiles for six major elements in coal-fired particulates at the scrubber outlet are depicted graphically in Figure 4-2. These profiles show that sulfur and carbon are more concentrated near the surface than deeper inside the particles. Both the sulfur and the carbon curves, however, level off after 275 Å. Hence, the thickness of the deposited layer of sulfur and carbon compounds appears to be approximately 275 Å. For sulfur, these data indicate that while there may be higher surface concentration of sulfur containing compounds in the particulates emitted from the scrubber, some of these compounds are probably deposited on particles composed of solid sulfate or sulfite. This would be the case if sulfuric acid condensed on the sodium bisulfate ($NaHSO_4$) or calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) particles that have been found to be present. For carbon, the depth profile data indicate that a fraction of the carbon, either as oil soot*, or as a carbon containing compound (such as carbonate or bicarbonate), could be deposited on the surface of the fine particulates emitted. The leveling off of the carbon curve, however, indicates that another fraction could be emitted as solid oil soot particles or solid

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* Oil soot deposited in the duct-work downstream of the boiler during oil firing.

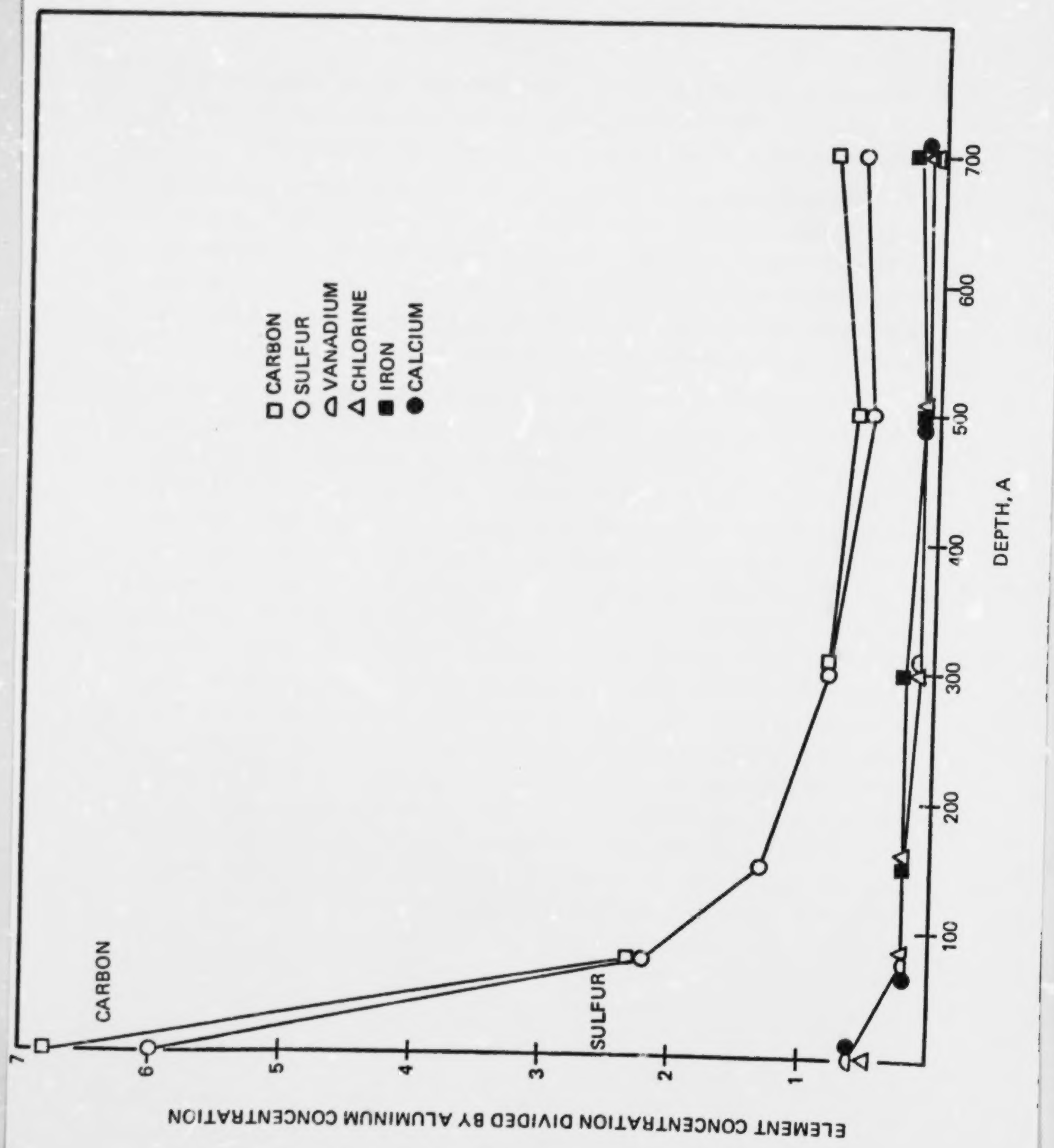

Figure 4-2. Depth profile analysis of outlet coal particulate - Test 201-1

carbonate/bicarbonate particles. The depth profile for iron, vanadium, chlorine, and calcium is reasonably flat and indicates that the relative concentrations of these elements remain approximately constant.

Although only low penetration analyses were performed on oil-fired particulates, available data indicate trends similar to those observed with coal fired particulates. Elements which appear to be enriched on the particulate surface include sulfur, phosphorous and carbon. On the other hand. vanadium and the typical ash components aluminum and silicon appear to be more concentrated in the bulk of the particulate matter.

The composition of particulate at the scrubber inlet and outlet has also been determined by PLM analyses. Estimated weight percentages of coal- and oil-fired particulate components are presented in Table 4-20. It may be noted that a substantial fraction of the coal-fired particulates at both the scrubber inlet and outlet is composed of oil soot. This is attributed to particulates deposited in the boiler during previous oil-fired operation and subsequent attrition during coal firing. The increase in weight percent of oil soot across the scrubber is consistent with results of ESCA analyses, as discussed previously. Both the PLM analysis and the ESCA analysis have shown that oil soot could be emitted as fine, solid particulates. Oil-fired particulates at the scrubber inlet are composed primarily of oil soot, various sulfate/sulfite compounds and fused ash while the outlet particulate is composed largely of sulfates and sulfites. Noting that the total quantity of particulate emissions after scrubbing is comparable for coal and oil firing, these data indicate that oil soot present during coal firing is finer than that generated during oil firing and is, therefore, not as efficiently removed by the scrubber. This is consistent with the observation made during PLM analyses that oil soot in coal particulate was fragmented while soot in oil particulates was present as cenospheres with only partial fragmentation.

Calcium sulfite hemihydrate and unknown sulfates comprise a principal portion of scrubber outlet sample for both fuels, 50 to 65% for coal particulate and 80 to 90% for oil particulate. These materials were also found to comprise 20 to 39% of the scrubber inlet particulates from oil firing. The $CaSO_3 \cdot 1/2\ H_2O$ and unknown sulfates identified at the scrubber

TABLE 4-20. MAJOR PARTICULATE COMPONENTS
DETERMINED BY PLM ANALYSIS*

Component	Approximate Weight %			
	Scrubber Inlet		Scrubber Outlet	
	Coal	Oil	Coal	Oil
Ash[†]				
Fused	15-30	13-23	---	---
Unfused	50-65	1-4	---	---
Minerals				
Fe_2O_3	1-5	< 1	15-25	8-16
Fe_3O_4 (Magnetite)	10-15	< 1	---	---
SiO_2	< 2	---	---	---
$CaCO_3$	---	≤ 3	1-5	---
Oil Soot	10-20	43-57	25-40	2-8
Coke	< 2	---	---	---
$CaSO_3 \cdot 1/2\ H_2O$ and Unknown Sulfate	---	20-39	50-65	80-90

[*] Coal-fired samples were taken from test 201-1. Oil-fired samples were taken from test 202-4.

[†] This is primarily composed of iron-aluminum silicates.

outlet during coal firing are mostly generated by the scrubber*. As discussed previously, the unknown sulfates may be composed primarily of sulfuric acid aerosol and sodium bisulfate. Sulfate data presented previously indicate that scrubber inlet oil particulates contain approximately 40% sulfate ion. Hence, the PLM estimate for $CaSO_3 \cdot 1/2\ H_2O$ and unknown sulfates weight percentages of 20 to 39% appear to be somewhat low. Further, the $CaSO_3 \cdot 1/2\ H_2O$ would appear to be present only as a minor constituent. This may indicate that tabulated inlet weight percentage of oil soot, the most difficult particulate component to quantify, is high with respect to the true particulate composition. Similarly, sulfate data indicate that outlet particulates are approximately 63% sulfate ion. Assuming that sulfate ions are combined with calcium or sodium, outlet particulates may consist of up to 92% sulfate compounds. Hence, $CaSO_3 \cdot 1/2\ H_2O$, if present in either the scrubber inlet or outlet, appears to be a minor constituent of particulates generated during oil firing.

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[*] Strictly speaking, $CaSO_3 \cdot 1/2\ H_2O$ is formed in the regeneration of Na_2SO_3 and a fraction of it is carried over with the regenerated Na_2SO_3 into the scrubber.

Chloride, Fluoride, and Nitrate Emissions

Specific anion analysis was performed on extracts from particulate catches from the Method 5 sampling train. Emissions data for chloride, fluoride, and nitrate are presented in Table 4-21. In the coal-fired test, chlorides and fluorides are removed with high degrees of efficiency, at greater than 99% and greater than 85%, respectively. These are to be expected because the overall removal efficiency of the trace element cations is greater than 99%. In the oil-fired case, the fluoride removal efficiency is high, 85 to 89%, and also corresponds to the trace element cation removal efficiency of 87%. The lower removal efficiencies for chlorides and nitrates in the oil fired test, about 51% and 57%, respectively, suggest that these anions may be associated with the finer particulate matter which is not efficiently removed by the scrubber.

Comparison of the coal and oil tests shows that considerably higher chloride and fluoride levels were emitted during coal firing. In the case of chloride, this is as expected, because of the higher chlorine level in the coal fuel. However, in the coal test, only 14% of the fuel chlorine was analyzed in the particulate extract from the scrubber inlet. It is possible that some of the chlorine is emitted in the form of acid vapors, which would not be detected by analysis of particulate extracts. The lower removal efficiency of chlorides in the oil fired test as compared to coal firing can be explained as resulting from the lower particulate removal efficiency for oil particulates.

TABLE 4-21. CHLORIDE, FLUORIDE, AND NITRATE EMISSIONS FROM COAL AND OIL FIRING

Fuel	Test	Cl^-			F^-			NO_3^-		
		Inlet ng/J	Outlet ng/J	Removal Efficiency, %	Inlet ng/J	Outlet ng/J	Removal Efficiency, %	Inlet ng/J	Outlet ng/J	Removal Efficiency, %
Coal	201-1	4.7	<0.004	>99	0.22	<0.03	>86	<0.48	<0.25	--
Oil	202-4	0.15	0.072-0.075	50-52	0.017	0.002-0.003	85-89	0.076	0.033	57

Comparison of fluoride and nitrate removal efficiencies for the coal and oil tests is not possible because several of the fluoride and nitrate concentrations were below the detection limit.

Organics

Four methods of analysis were utilized in determining flue gas organic loadings. Continuous FID analyses were performed to determine total organic concentrations assuming all carbon to be present as methane. Bag samples of gas were collected over a 30 to 45 minute period and were analyzed for organics in the C_1 to C_6 range using a field chromatograph. A laboratory chromatograph was employed to determine hydrocarbons in the C_7 to C_{16} range in samples obtained from the SASS train (GC/TCO). SASS train samples were also analyzed gravimetrically for higher molecular weight organics. For identification of organic compounds, infrared spectroscopy analysis (IR) and low resolution mass spectrometry (LRMS) were performed on residues from gravimetric analysis, and samples from a modified Method 5 sampling train (with an XAD-2 resin module) and from gas bags were analyzed by gas chromatography/mass spectrometry (GC/MS).

For C_1 to C_{16} organics, the subscripted carbon number refers to a boiling range rather than a specific molecular structure. The approximate boiling ranges corresponding to each carbon are presented in Table 4-22. A comparison of organic determinations for the coal- and oil-fired tests is presented in Table 4-23. Analytical results for the outlet resin samples from the SASS train were not available, so these were calculated using data from four oil-fired and ten coal-fired boiler tests which used similar sampling trains, and assuming the proportion of organic material in the resin sample to the rest of the material trapped in the sampling train to be constant. These calculated values are good to a factor of 3 to 4.

Total organics determined as methane by FID show a slight increase across the scrubber for both oil and coal firing. As mentioned previously, this increase was determined to be statistically significant during the coal-fired test but insignificant during the oil-fired test. The reason for the increase is not known at this time. Organics in the C_1 to C_6 range were present, if at all, at sufficiently low concentrations that in both tests they were not detected by the field chromatograph. In the range of C_7 and above, the concentration of higher molecular weight organics was greater than the concentration of volatiles.

TABLE 4-22. APPROXIMATE BOILING RANGES CORRESPONDING TO EACH CARBON NUMBER

Carbon Number	Approximate Boiling Range	Carbon Number	Approximate Boiling Range
C_1	-160 to -100°C	C_9	140 to 160°C
C_2	-100 to - 50°C	C_{10}	160 to 180°C
C_3	- 50 to 0°C	C_{11}	180 to 200°C
C_4	0 to 30°C	C_{12}	200 to 220°C
C_5	30 to 60°C	C_{13}	220 to 240°C
C_6	60 to 90°C	C_{14}	240 to 260°C
C_7	90 to 110°C	C_{15}	260 to 280°C
C_8	110 to 140°C	C_{16}	280 to 300°C

TABLE 4-23. COMPARISON OF ORGANIC DETERMINATIONS DURING COAL AND OIL FIRING

Method	Coal Fired				Oil Fired			
	Test	Inlet	Outlet	% Change	Test	Inlet	Outlet	% Change
Total as CH_4 (Continuous FID)	200	3.8	4.6	Not Significant	202-1	2.9	3.3	Not Significant
C_1 - C_6 (GC on Bag Samples)	200	≤5.4	≤5.4	---	202-1	≤4.6	≤4.6	---
C_7 - C_{16} (GC on SASS Train Samples)	200	0.34	0.27*	-20	203	0.17	0.02*	-85
$>C_{16}$ (Gravimetric on SASS Train Samples)	200	2.3	0.33*	-85	203	2.6	0.43*	-83

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*The values for the resin sample are calculated (see text).

Comparison of the oil and coal-fired results shows essentially no difference in the organic loadings from the two fuels. The rough distributions of molecular weights are also very similar. The scrubber removal efficiencies show some variation: 20% for the C_7 to C_{16} fraction, coal fired, and 83 to 85% for the other fractions for which efficiencies could be calculated. However, since the outlet concentrations for the C_7 and above fractions are good within a factor of 3 to 4, the efficiencies presented actually represent rather wide ranges. Because the outlet value for coal organics in the C_7 to C_{16} range is 80% of the inlet value, the factor of 3 to 4 uncertainty means that the 20% efficiency actually represents a range of 0 to 97%. Since the outlet values for the other fractions are much lower, their uncertainty affects the calculated removal efficiency less: 85% actually represents a range of 50 to 98%. Hence, a conclusive comparison of the C_7 to C_{16} removal efficiencies for coal and oil firing cannot be made.

Results of IR analysis on the fractionated XAD-2 resin extracts from SASS train samples are presented in Table 4-24. As can be seen, the blank contained many organic materials presumably released by the resin. This was a source of difficulty in interpreting analytical results, especially because the amount of resin-generated material seemed to vary from sample to sample. IR analysis of several of the LC fractions did not identify any compounds which could be directly associated with combustion.

Table 4-25 summarizes the organics that were identified in gas bag samples by GC/MS analysis. Again, none of the compounds is directly associated with combustion. They are, however, representative of the types of compounds that are used in the manufacture of the sample bags and the solvents used in the analysis. This finding is consistent with GC, gravimetric, and FID analyses indicating low organic emissions.

TABLE 4-24. SUMMARY OF THE INFRARED ANALYSIS OF ORGANICS FROM OIL AND COAL COMBUSTION

Total Organics, mg/m^3	LC1			LC2*			LC3			LC4			LC5			LC6			LC7			Total		
	Coal	Oil	Blank	Coal	Oil	Blank	Coal	Oil	Blank	Coal	Oil	Blank*	Coal	Oil	Blank	Coal	Oil	Blank	Coal	Oil	Blank	Coal	Oil	Blank
	0.14	0.39	0.02				0.06	0.05	0.03	0.12	0.03	0.01	0.37	0.04	0.02	0.95	0.28	0.10	0.06	0.02		1.70	0.51	0.18
Category	Intensity																							
Aliphatic Hydrocarbons	XM	XM	XM				XM	XM	XM	Xm				Xm	Xm		Xm				Xm			
Aromatic Hydrocarbons	Xm	Xm	Xm				XM	XM	XM	XM	Xm		Xm	Xm	Xm		Xm				Xm			
Chlorinated Hydrocarbons																Om								
Silicones							Xm			Xm				Xm	Xm		Xm							
Heterocyclic Sulfur Compounds										Xm			Xm	Xm			Xm			Xm				
Thiocarbonyl Compounds										Xm														
Nitro Compounds										XM			Xm	OM	Om					Om	Om			
Ethers										XM														
Esters									Xm	XM	XM		XM	XM	XM	XM	XM	XM	XM	XM	Xm			
Amides																Xm			Om	OM	Om			
Alcohols																Xm			Xm					
Glycols																	XM	XM		XM	XM			
Phenols										Xm						[illegible]	[illegible]	[illegible]	OM					
Carboxylic Acids										Xm						XM	XM	XM	XM	XM	XM			
Sulfonic Acids																				XM				
Silicates									XM															

*Not Analyzed.

O = At least one species suspected present.
X = At least one species present.

M = Major Component.
m = Minor Component.

TABLE 4-25. COMPARISON OF ORGANIC COMPOUNDS IDENTIFIED BY GC/MS IN THE FLUE GAS DURING COAL AND OIL FIRING

Compound	Emission Rate, ng/J							
	Coal Fired				Oil Fired			
	201-2		201-3		202-2		202-3	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Propionaldehyde	0.075	0.17	0.024	--	0.075	--	0.052	--
Nitromethane	--	--	--	--	--	--	0.023	--
Ethyl-n-butyl ether	0.88	0.66	0.400	0.66	0.64	--	0.37	--
Ethyl acetate	--	--	--	--	--	--	--	0.85
Hydrocarbon (C_6H_{14})	--	--	0.17	--	--	--	--	--
Chloropropanol	--	--	--	0.0017	--	--	--	--
4-methyl-3-pentene-2-one	--	--	--	--	--	0.21	0.13	0.01
Unidentified alcohol	--	0.0018	--	--	--	--	--	--
Octanol	--	--	--	--	--	--	0.017	--
Ketone (MW 138)	--	--	--	--	--	--	0.0074	--
Ketone (MW 140)	0.0017	--	0.003	--	0.0053	--	--	--
Phthalic anhydride	--	--	--	--	--	--	0.011	--
Amyl benzoate	--	--	--	--	--	0.0006	--	--
Glycerol triacetate	--	--	--	--	--	--	0.016	--
Methyl substituted aromatic	0.00075	--	--	--	--	--	--	--

Polycyclic Organic Material

Polycyclic organic material (POM) was not found in the scrubber inlet or outlet samples at detection limits of 0.3 $\mu g/m^3$ during either coal or oil firing. This observation is consistent with the findings to date from the EPA sponsored project "Emissions Assessment of Conventional Combustion Sources". However, two POM compounds for which MATE values are below 0.3 $\mu g/m^3$ are benzo(a)pyrene and dibenz(a,h)anthracene. The MATE values for benzo(a)pyrene and dibenz(a,h) anthracene are 0.02 $\mu g/m^3$ and 0.09 $\mu g/m^3$, respectively. While available data indicate that many POM compounds are not present at concentration greater than or equal to their MATE value during oil firing, additional analyses at higher GC/MS sensitivity would be required to conclusively preclude the presence of all POMs at concentrations above their MATE values.

Scrubber Efficiency

Flue gas analyses indicate that scrubber processing removes significant percentages of flue gas sulfur oxides (SO_2, SO_3, and $SO_4^=$), total particulates and organics in the boiling range of C_7 and higher. Scrubber removal efficiency data for these flue gas components are summarized in Table 4-26. The average removal efficiencies for both coal and oil fired tests have been discussed and compared in previous subsections. However, it is important to note that it is the C_7 and higher hydrocarbons which are removed with the efficiencies listed. These fractions comprise 38 to 96% and 32 to 69% of the organics measured at the scrubber inlet for the oil- and coal-fired tests, respectively. Hence, based on the total organics generated, removal efficiencies of 32 to 84% for oil and 25 to 53% for coal were obtained. Although the average values for coal were lower than the oil, these values were calculated using the 20% removal figure for coal C_7 to C_{16} organics. As discussed previously, this 20% efficiency for coal firing has a higher uncertainty than the 85% value for oil firing and, therefore, these efficiencies cannot be reasonably compared. Other than the inconclusive removal efficiency for C_7 to C_{16} coal-fired organics, the data indicate that removal efficiency of organics greater than C_7 is 83-85% and is essentially identical for coal and oil firing.

TABLE 4-26. SCRUBBER EFFICIENCY DURING COAL AND OIL FIRING

Fuel	Test Number	SO_2	SO_3	$SO_4^=$	Total Particulates	C_7 to C_{16} Organics	C_{17} and Higher Organics
Coal	200	97	--	--	99	20	85
	201-1	97	33	88	99	--	--
	201-2	97	--	--	--	--	--
	201-3	97	--	--	--	--	--
	201-4	95	32	--	99	--	--
	Average	97	32	88	99	20	85
Oil	202-1	97	29	--	88	--	--
	202-2	97	--	--	--	--	--
	202-3	97	--	--	--	--	--
	202-4	98	28	60	75	--	--
	203	--	--	--	--	85	83
	Average	97	29	60	82	85	83

It is not known by what process organics are so efficiently removed. There are, however, at least three possible mechanisms:

- Sorption - Some organics could adsorb on particulates.
- Condensation - High-boiling organics could condense and be removed as "particulates".
- Dissolution - Some organics are partially water soluble. These compounds could be removed by dissolving in the slurry.

One or any number of these mechanisms may account for the high removal efficiency of organics.

LIQUID WASTE

As discussed previously, only one significant waste water stream is produced. The stream is a combination of water treatment waste, boiler blowdown, and acid waste water from elsewhere in the manufacturing facility. The quality of this combined stream is such that it is acceptable for disposal into the municipal sewer system. Liquid streams from the scrubber operation are passed to the thickener and recirculated to the scrubber after the filtration step. There is no direct wastewater discharge from the scrubber operation, as the process is designed to dispose of all of the water that enters its system through evaporation and moisture entrained in the scrubber cake.

Because several streams are mixed together, it is not possible to accurately determine what part of the effluent is attributable to the boiler. However, the flow rate of the combined stream is approximately 10,000 liters/hr (40 gallons/min).

Water Quality Parameters

Table 4-27 summarizes the waste water parameters for the combined waste water streams analyzed during coal and oil firing. Note that these values do not represent water produced solely by the boiler but also include process waste.

Inorganics - Combined Waste Water Stream

Analyses of major inorganic cations in the combined waste water stream during coal and oil firing are presented in Tables 4-28 and 4-29. These data are based on the SSMS technique which is accurate to within a factor of approximately 3. Of the elevn elements analyzed, none exceeds its MATE value for either fuel based on health considerations. However, based on the factor of 3 uncertainty in SSMS analyses, cobalt, nickel, copper and cadmium may exceed their respective ecological MATE values during coal firing. Similarly, nickel and copper may exceed their ecological MATE values during oil firing.

TABLE 4-27. COMBINED STREAM WASTE WATER PARAMETERS

Test	pH	Hardness (as $CaCO_3$), mg/l	Alkalinity (as $CaCO_3$), mg/l	Cyanide, mg/l
		COAL FIRING		
200	7.9	210	115	0
201-1	7.5	158	125	0
201-2	8.2	135	130	0
201-3	8.0	145	125	0
201-4	7.3	100	145	0
Average	7.8 ± 0.4	150 ± 40	128 ± 11	0
		OIL FIRING		
202-1	7.5	105	135	0
202-2	6.5	140	65	0
202-3	7.5	155	120	0
202-4	6.5	150	50	0
203	6.9	110	140	0
Average	7.0 ± 0.5	132 ± 23	102 ± 42	0

TABLE 4-28. WASTE WATER INORGANICS FOR COAL FIRING

Trace Element	mg/l	g/hr*	MATE Value, mg/l		Degree of Hazard	
			Health	Ecology	Health	Ecology
Be	<0.001	<0.01	0.030	0.055	<0.033	<0.018
F	0.8	8	38	--	0.021	--
V	0.003	0.03	2.5	0.15	0.0012	0.02
Cr	0.002	0.02	0.25	0.25	0.008	0.008
Co	0.1	1	0.75	0.25	0.13	0.40
Ni	0.005	0.5	0.23	0.010	0.022	0.50
Cu	0.02	0.2	5.0	0.050	0.004	0.40
Sr	0.5	5	46	--	0.011	--
Cd	<0.001	<0.01	0.050	0.001	<0.02	<1.0
Sb	<0.001	<0.01	7.5	0.20	<0.0001	<0.005
Pb	0.01	0.1	0.250	0.050	0.04	0.20

* Flow rate of 10,000 liters per hour, combined waste water.

TABLE 4-29. WASTE WATER INORGANICS - OIL FIRING

Element	mg/l	g/hr*	MATE Value, mg/l		Degree of Hazard	
			Health	Ecology	Health	Ecology
Be	<0.001	<0.01	0.030	0.055	0.033	0.018
F	4	40	38.0	--	0.100	--
V	0.002	0.02	2.50	0.150	0.001	0.013
Cr	0.02	0.02	0.250	0.250	0.080	0.080
Co	0.007	0.07	0.750	0.250	0.009	0.028
Ni	0.02	0.2	0.230	0.010	0.087	2.00
Cu	0.02	0.2	5.0	0.050	0.004	0.400
Sr	0.3	3	46.0	--	0.007	--
Cd	<0.001	<0.01	0.050	0.010	<0.02	<0.004
Sb	0.001	0.01	7.50	0.200	0.0001	0.005
Pb	0.006	0.06	0.250	0.050	0.024	0.005

*Flow rate of 10,000 liters per hour.

Organics - Combined Waste Water

Concentrations of C_7 to C_{16} organics measured in the combined waste water stream are summarized in Table 4-30. High molecular weight organics ($>C_{16}$) were detected at a concentration of 0.21 mg/liter during coal firing, but these are probably attributable to process wastes generated at the manufacturing site. High molecular weight organics were not detected during oil firing. The only organics detected were the C_{10}, C_{12}, C_{14} and C_{15} fractions during coal firing and the C_{10}, C_{14} and C_{15} fractions during oil firing. Each of these fractions was detected at or below the 0.1 mg/liter level yielding a total output of C_7 to C_{16} organics of 0.4 mg/liter during coal firing and less than 0.3 mg/liter during oil firing. As a basis for comparison, the water MATE values for alkanes, alkenes and alkynes are in the 500 to 14,000 mg/liter range based on human health considerations and in the 1.0 to 100 mg/liter range based on ecological considerations. Discharge concentrations of organics in the combined waste water stream are well within these MATE values for both coal and oil firing.

SOLID WASTE

Three solid waste streams are produced by the system:

- Bottom ash;
- Fly ash;
- Scrubber cake.

Approximate quantities of bottom ash and scrubber cake produced during coal and oil firing are presented in Table 4-31. Only small quantities of fly ash were collected during the test period due to malfunction of the multiclone. The quantity of bottom ash produced during coal firing is at least a factor of 80 larger than that produced during oil firing due to the difference in fuel ash contents (9.9% for coal versus 0.02% for oil). Similarly, the quantity of scrubber cake generated during coal firing is up to 3 times greater than was produced during oil firing. This difference would be reduced by proper multiclone operation and the attendant reduction in solids content of the scrubber cake during coal firing.

TABLE 4-30. SUMMARY OF C_7 - C_{16} ORGANICS IN THE WASTE WATER

Carbon Number	mg/l Coal Firing	mg/l Oil Firing	Carbon Number	mg/l Coal Firing	mg/l Oil Firing
C_7	ND*	ND	C_{13}	ND	ND
C_8	ND	ND	C_{14}	0.1	< 0.1
C_9	ND	ND	C_{15}	0.1	< 0.1
C_{10}	0.1	< 0.1	C_{16}	ND	ND
C_{11}	ND	ND			
C_{12}	ND	ND	Total C_7 - C_{16}	0.4	< 0.3

*ND means none detected.

TABLE 4-31. SOLID WASTE PRODUCTION RATES

Test	Bottom Ash kg/hr	Bottom Ash µg/J	Scrubber Cake† kg/hr	Scrubber Cake† µg/J
		COAL FIRING		
200	∿80*	∿753	1100	10.2
201-1	∿80	∿763	1100	10.5
201-2	∿80	∿735	1200	11.0
201-3	∿80	∿857	850	9.1
201-4	∿80	∿738	840	7.8
		OIL FIRING		
202-1	< 1	< 7.4	400	2.9
202-2	< 1	< 7.4	550	4.1
202-3	< 1	< 7.6	380	2.9
202-4	< 1	< 8.3	Not Measured	
203	< 1	<11.1	Not Measured	

*15 tons per week

†Scaled up to represent scrubbing of 100% of the flue gas for boiler No. 4.

The scrubber cake produced after filtration has the appearance of a clayey silt. Its grain size is quite uniform and characteristic of silty soils, but its behavior closely resembles a clay in many respects. As obtained from the vacuum filter, the scrubber cake consists of small lumps and appears to be relatively dry; in actuality, however, the water content generally ranges from about 30 to 50%.

Assuming that calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) is the principal product from SO_2 scrubbing and Na_2SO_3 regeneration, data presented in Table 4-32 represent the estimated composition of scrubber cake produced during coal and oil firing. Scrubber cake produced during coal firing appears to be composed of 29% fly ash, 24% $CaSO_3 \cdot 1/2\ H_2O$ and 39 to 46% of unbound water. However, if the multiclone had been functioning properly during the test period, more fly ash would be removed upstream of the scrubber and the fly ash content of the scrubber cake would be lowered proportionally. The amount of cake produced could be reduced to 600-750 kg/hr, on a wet basis, assuming a multiclone efficiency of approximately 60 to 80%.

Although the scrubber cake production rate was not measured for test 202-4, it has been estimated as the average of production rates determined for other oil-fired tests performed. Data presented in Table 4-32 indicate that the scrubber cake produced during oil firing is composed of 44 to 50% unbound water and at least 47% calcium sulfite hemihydrate. These data reflect the low particulate emissions which are characteristic of oil firing. Only 1% of the scrubber cake is estimated to be particulate. Assuming the percentage of unbound water associated with scrubber cake particulate to be the same as the percentage for scrubber cake as a whole, reduction of the particulate content of the coal firing scrubber cake to 1% yields approximately 500 kg/hr of low particulate cake. This corresponds well with the oil firing scrubber cake production rate of 443 kg/hr.

Although the scrubber cake material is composed predominantly of relatively insoluble solids (calcium sulfite, calcium sulfate, and some calcium carbonate), the intersititial water does contain soluble residues of lime, sulfate, sulfite and chloride salts. Trace elements in the fly ash may also contribute to the leachate from the disposed scrubber cake and are of special concern. The concentrations of 20 trace elements in the scrubber cake during coal and oil firing are presented in Tables 4-33 and

TABLE 4-32. ESTIMATED SCRUBBER CAKE MASS BALANCE

Component	Contribution to Scrubber Cake kg/hr Coal*	Contribution to Scrubber Cake kg/hr Oil*	Contribution to Scrubber Cake Weight % Coal*	Contribution to Scrubber Cake Weight % Oil*
Fly Ash Removed by Scrubber	324	5	29	1
$CaSO_3 \cdot 1/2\ H_2O$ Formed from SO_2 Scrubbing and Na_2SO_3 Regeneration	262	210	24	47
$CaSO_4$, $CaCO_3$, Na_2SO_3, $Ca(OH)_2$ $NaHSO_4$ and Na_2SO_4 Losses (Estimated)	10-85	6-35	1-8	1-8
Water	429-504	193-222	39-46	44-50
Total	1,100	443†	100	100

*Coal firing data are from test 201-1 and oil firing data are from test 202-4.

†Total cake production rate was estimated from the average of tests 202-1, 202-2 and 202-3.

4-34. With respect to human health based MATE values for solids, boron is the only trace element from coal firing which does not exceed its MATE value, and antimony, boron, molybdenum and zinc do not exceed MATE values during oil firing. With respect to ecology based MATE values for solids, all trace elements from coal and oil firing exceeded their MATE values with the exception of boron and molybdenum which did not exceed their MATE values during oil firing. This is a consequence of transforming a high volume, low concentration pollution stream to a low volume, high concentration stream which can be more readily contained. The degree of hazard for most of the trace elements in these scrubber cakes is sufficiently high to warrant the disposal of these solid wastes in specially designed landfills.

The concentrations of 20 trace elements present in the coal firing fly ash are presented in Table 4-35. Again, in almost every case, the trace element concentration in the fly ash has far exceeded its MATE value for solids. Trace element concentrations in the bottom ash would be similar to those of the fly ash, except that the more volatile elements and the elements that form volatile compounds would be more enriched in

TABLE 4-33. INORGANIC CONTENT OF SCRUBBER CAKE FROM COAL-FIRING (DRY BASIS) - TEST 201-1

Element	Concentration μg/g	MATE Value, μg/g		Degree of Hazard	
		Health	Ecology	Health	Ecology
Ca	60,715	480	32	126	1,897
Mg	1,458	180	174	8.1	8.4
Sb	315	15	0.4	21	788
As	532	0.5	0.1	1,064	5,320
B	88	93	50	0.9	1.8
Cd	13	0.1	0.002	130	6,500
Cr	141	0.5	0.5	282	282
Co	424	1.5	0.5	283	848
Cu	112	10	0.1	11	1,120
Fe	47,241	3.0	0.5	15,738	94,482
Pb	297	0.5	0.1	594	2,970
Mn	51	0.5	0.2	102	255
Mo	1,117	150	14	7.4	80
Ni	114	0.45	0.02	253	5,700
V	195	5.0	0.3	39	650
Zn	282	50	0.2	5.6	1,410
Se	256	0.10	0.05	2,560	5,120
Sr	642	92	--	7.0	--
Al	45,310	160	2.0	283	22,655
Zr	106	15	--	7.1	--
Total	159,409				

TABLE 4-34. INORGANIC CONTENT OF SCRUBBER CAKE FROM OIL FIRING (DRY BASIS) - TEST 202-4

Element	Concentration µg/g	MATE Value, µg/g		Degree of Hazard	
		Health	Ecology	Health	Ecology
Ca	200,000	480	32	417	6,250
Mg	3,799	180	174	21	22
Sb	3*	15	0.4	0.2	7.5
As	15*	0.5	0.1	30	150
B	40	93	50	0.4	0.8
Cd	1*	0.1	0.002	10	500
Cr	15	0.5	0.5	30	30
Co	19*	1.5	0.5	13	38
Cu	16	10	0.1	2	160
Fe	2,164	3.0	0.5	721	4,328
Pb	6*	0.5	0.1	12	60
Mn	6	0.5	0.2	32	80
Mo	14*	150	14	0.1	1
Ni	132	0.45	0.02	293	6,600
V	203	5.0	0.3	41	677
Zn	36	50	0.2	0.7	180
Se	9*	0.10	0.05	90	180
Sr	239	92	--	2.6	--
Al	1,684	160	2.0	11	842
Zr	37	15	--	2.5	--
Total	208,450				

*SSMS analyses were utilized where ICPOES analysis provided upper limit data only.

TABLE 4-35. INORGANIC CONTENT OF FLY ASH FROM COAL-FIRING - TEST 201-1

Element	Concentration µg/g	MATE Value, µg/g		Degree of Hazard	
		Health	Ecology	Health	Ecology
Ca	378	480	32	0.8	12
Mg	2,478	180	174	14	14
Sb	438	15	0.4	29	1,095
As	1,015	0.5	0.1	2,030	10,150
B	20	93	50	0.2	0.4
Cd	18	0.1	0.002	180	9,000
Cr	434	0.5	0.5	868	868
Co	408	1.5	0.5	272	816
Cu	320	10	0.1	32	3,200
Fe	129,330	3.0	0.5	43,110	258,660
Pb	438	0.5	0.1	876	4,380
Mn	121	0.5	0.2	242	605
Mo	1,288	150	14	9	92
Ni	165	0.45	0.02	367	8,250
V	376	5.0	0.3	75	1,253
Zn	179	5.0	0.2	36	895
Se	378	0.10	0.05	3,780	7,560
Sr	728	92	--	8	--
Al	109,450	160	2.0	684	54,725
Zr	187	15	--	12	--
Total	248,149				

the fly ash. Thus, the concentrations of arsenic, antimony, boron, chromium, manganese, nickel, vanadium, zinc, selenium and zirconium would all be lower in the bottom ash. Oil firing produces little or no fly ash and bottom ash. As such, insufficient material was available to warrant analysis.

An overall mass balance for the 20 trace elements has been performed for coal and oil firing tests. Mass balance results are presented in Tables 4-36 and 4-37 for coal and oil firing, respectively. The percent of the trace element in the fuel feed that could be located in the effluent streams (i.e., scrubber cake and scrubber effluent gas for oil firing) is used as a measure of mass balance closure. With the exception of boron, copper, strontium and zirconium, very good mass balance closure was obtained for trace elements from coal firing. These data support the reliability and accuracy of sampling and analysis of trace elements and flow rate measurements.

Although good mass balance closure was obtained for many trace elements from oil firing, closure was not generally as good as was observed during coal firing. This is not entirely unexpected since concentrations of most trace elements in fuel and effluent streams are substantially lower during oil firing than during coal firing (Refer to Tables 4-4, 4-33 and 4-34). Good mass balance closure was obtained for arsenic, boron, chromium, cobalt, copper, molybdenum, nickel, vanadium, zinc and selenium. Elements for which effluent flow rates substantially exceeded input feed rates, such as iron and aluminum, may show inordinately high concentrations in the scrubber cake due to the extremely high levels attained during coal firing and subsequent contamination of the recycle scrubber solution. Magnesium is the only element for which a poor mass closure cannot be attributed to either very low element concentrations or possible contamination of the scrubber solution during coal firing. Available analysis indicate that magnesium was discharged in the scrubber cake at a constant rate during both coal and oil firing. Although this observation may result from changes in the scrubber lime feed, a conclusive explanation is not available based on existing data.

TABLE 4-36. MASS BALANCE ON TRACE ELEMENTS - TEST 201-1

Element	Coal Feed g/hr	Scrubber Cake g/hr	Scrubber Effluent Gas g/hr	Bottom and Fly Ash[*] g/hr	Percent Recovery[†]
Ca	2,794	40,072	1.6	30	[‡]
Mg	1,270	962	0.5	198	91
Sb	308	208	1.1	35	79
As	497	351	9.7	81	89
B	8.7	58	1.2	1.6	700
Cd	12.7	8.6	0.04	1.4	79
Cr	174	93	5.7	35	77
Co	461	280	0.53	33	68
Cu	261	74	0.88	26	39
Fe	44,455	31,179	110	10,346	94
Pb	308	196	0.92	35	75
Mn	44	34	0.68	9.7	100
Mo	1,063	737	1.2	103	79
Ni	134	75	2.8	13	68
V	171	151	2.5	30	107
Zn	203	186	2.1	14	100
Se	265	169	4.3	30	77
Sr	247	424	2.5	58	196
Al	50,806	29,905	110	8,756	76
Zr	980	70	0.79	15	9

[*] For mass balance calculations, bottom ash has been assumed to have the same trace element concentrations as fly ash. This is an approximate assumption, as some trace elements are enriched in the fly ash.

[†] Percent recovery is defined as the ratio of the sum of the emissions for a trace element to the trace element in the coal feed.

[‡] Percent recovery for calcium is not calculated because most of the calcium in the scrubber cake is from the lime slurry.

TABLE 4-37. MASS BALANCE OF TRACE ELEMENTS - TEST 202-4

Element	Oil Feed g/min	Scrubber Cake g/min	Scrubber Outlet g/min	Percent[‡] Recovery
Ca	16.4	50,000	2.8	[**]
Mg	(12.2)[†]	950	1.2	>1,000
Sb	(2.4)	0.8[*]	0.2	42
As	(5.9)	3.9[*]	1.2	68
B	(20.9)	10.0	1.5	55
Cd	(11.0)	0.2[*]	2.6	25
Cr	3.6	3.9	0.7	125
Co	(3.9)	4.7[*]	0.5	133
Cu	4.2	4.1	0.3	105
Fe	36.7	541	11.0	>1,000
Pb	(7.9)	1.5[*]	0.5	25
Mn	(1.2)	4.0	0.2	350
Mo	(8.7)	3.5[*]	1.0	52
Ni	47.7	33.0	7.9	91
V	108.8	50.7	32.3	76
Zn	8.9	9.1	2.7	133
Se	(2.0)	2.4[*]	0.2	136
Sr	0.7	59.8	0.04	>1,000
Al	10.4	421	18.9	>1,000
Zr	(0.6)	9.2	0.04	>1,000

[*] SSMS data were utilized where ICPOES analysis provided upper limit data only.

[†] ICPOES data from the analysis of scrubber inlet particulates were utilized when fuel analysis provided upper limit data only.

[‡] Percent recovery of a trace element is 100 times the ratio of its total emission rate (scrubber cake plus scrubber outlet) to its feed rate.

[**] Percent recovery for calcium is not calculated because most of the calcium in the scrubber cake is from the lime slurry.

Scrubber cakes from coal and oil firing were also analyzed for organics but none were detected. This is to be expected since the concentration of organics in the flue gas streams was extremely low.

ANNUAL EMISSIONS

Estimated annual controlled and uncontrolled emissions of the major pollutants are presented in Table 4-38 for both fuels. These estimates were computed assuming that the boiler operates at 100% load for 87% of the year (7,560 hours/year) and that either coal or oil is the only fuel burned.

AIR QUALITY ASSESSMENT - COAL AND OIL FIRING

Simplified air quality models were used to determine relative air quality resulting from uncontrolled and controlled emissions. The ambient air quality values are approximate only. The emphasis should be placed on the relative values for each case as opposed to their absolute values.

Worst case weather conditions and typical weather conditions were considered. The worst case was assumed to be plume trapping. An equation proposed by Bierly and Hewson [14] was used with the following assumptions: inversion height 100 meters, wind speed 1.0 meter/second, D class stability (neutrally stable) in the mixing layer, and effective stack height of 50 m (1640 ft). The typical case was assumed to correspond to the standard Gaussian convective diffusion equation, [15]. The following conditions were used: wind speed 4.0 meters/second and D class stability. These conditions could reasonably be expected to occur almost anywhere in the country. Typical does not mean average. It was assumed that all species were inert. No photochemical reactions were considered. (See Appendix A for details).

Figures 4-2 through 4-9 present plots of approximate ambient air quality as a function of distance downwind from a single 10 MW equivalent source. Data for NO_x, CO, SO_2 and particulates are presented. The purpose of these figures is not to attempt to accurately predict air quality but to compare the effects of controlled and uncontrolled emissions under an

TABLE 4-38. ANNUAL EMISSIONS*

TABLE 4-38. ANNUAL EMISSIONS*

	Pollutant	kg/year					
		Scrubber Inlet			Scrubber Outlet		
		Coal Firing	Oil Firing	Coal/Oil	Coal Firing	Oil Firing	Coal/Oil
Gaseous	NO_x (as NO_2)	500,810	164,230	3.05	442,520	157,390	2.81
	SO_2	1,127,300	906,202	1.24	36,800	24,453	1.51
	SO_3	6,184	7,249	0.85	4,157	5,183	0.80
	$SO_4^=$	67,214	20,894	3.22	8,110	8,303	0.98
	CO	16,119	4,991	3.23	14,497	4,845	2.99
	Organics (as CH_4)	5,870	2,272	2.58	6,377	2,500	2.55
	$C_1 - C_6$[†]	<5,606	<4,164	--	<5,606	<4,164	--
	$C_7 - C_{16}$	345	155	2.22	274	18	15.2
	$>C_{16}$	2,311	2,381	0.97	335	392	0.85
	Total Particulates	2,991,700	53,832	55.6	18,856	13,686	1.38
	<1μ	--	--	--	11,691	11,359	1.03
	1 - 3μ	--	--	--	5,657	1,642	3.45
	3 - 10μ	--	--	--	1,320	634	1.93
	>10μ	--	--	--	188	0[‡]	--
		m^3/year					
Liquid	Blowdown/Waste Water	~76,000	~76,000	~ 1	~76,000	~76,000	~ 1
	Cooling Water	~86,000	~86,000	~ 1	~86,000	~86,000	~ 1
		kg/year					
Solid	Bottom Ash	~ 778,600	~ 7,600	~103	~ 778,600	~ 7,600	~103
	Fly Ash	~1,800,000	~15,000	~120	~1,800,000	~15,000	~120
	Scrubber Cake	0	0	--	8,054,100	3,011,000	2.67

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[*] Assuming 100% load, 45 weeks per year (7,560 hrs/year).

[†] These values represent the detection limit of the instrument used.

[‡] These values represent oil firing particulate with a minimum of coal ash contamination.

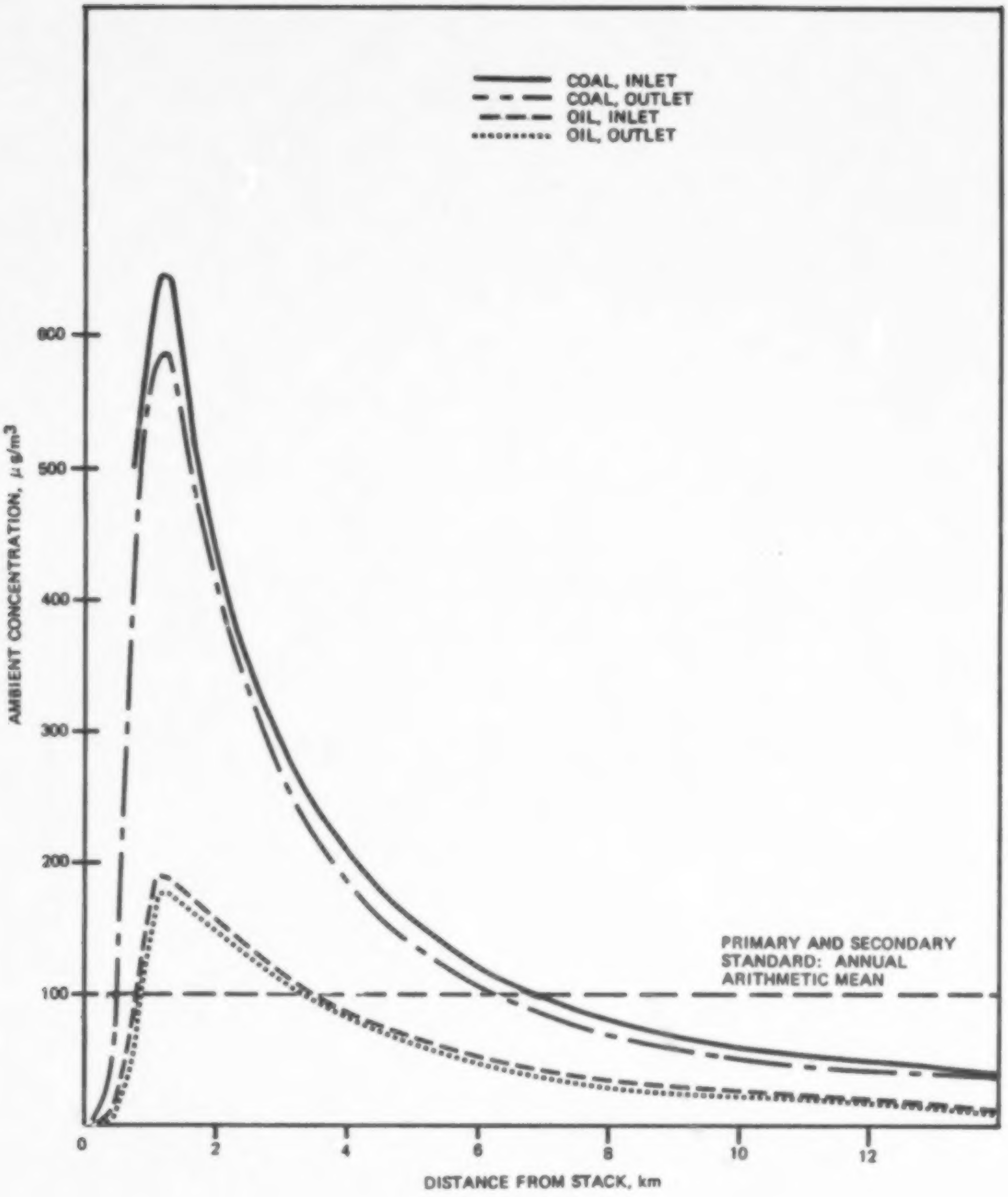

Figure 4-2. Comparison of NO_x Air Quality Resulting From Coal and Oil Firing Under Worst Case Weather Conditions (Tests 201-1 and 202-1)

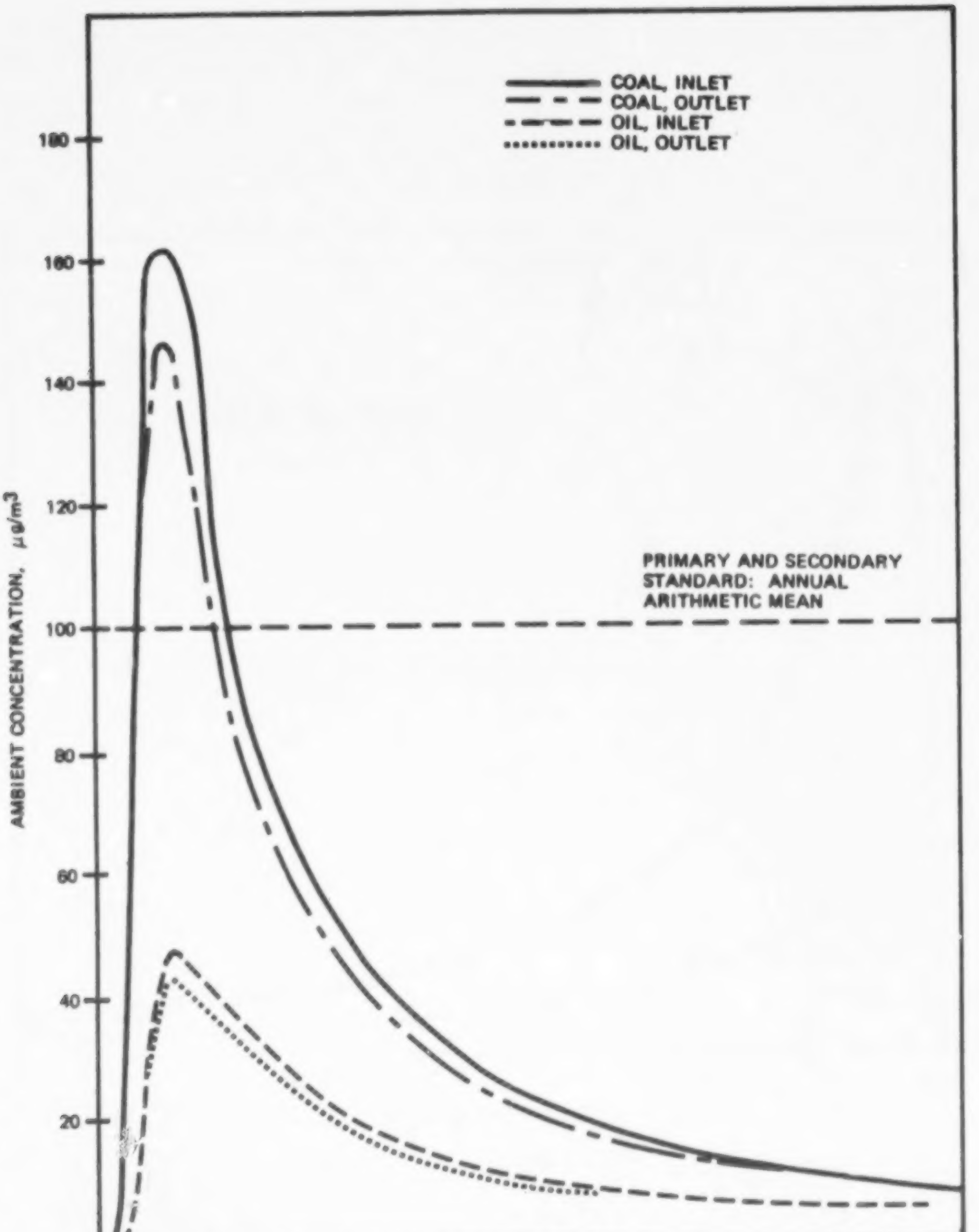

Figure 4-3. Comparison of NO_x Air Quality Resulting From Coal and Oil Firing Under Typical Weather Conditions (Tests 201-1 and 202-1)

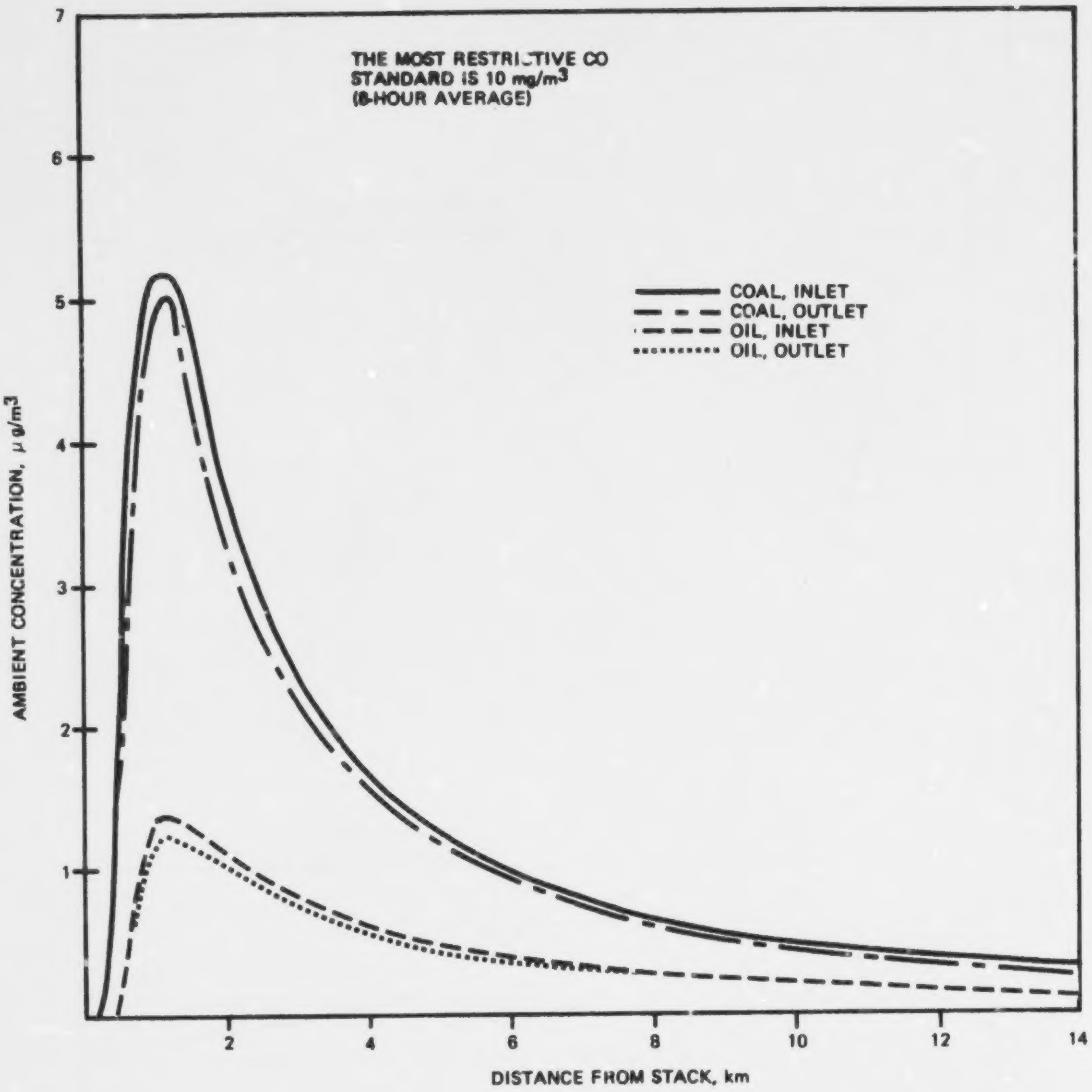

Figure 4-5. Comparison of CO Air Quality Resulting From Coal and Oil Firing Under Typical Weather Conditions (Tests 201-1 and 202-1)

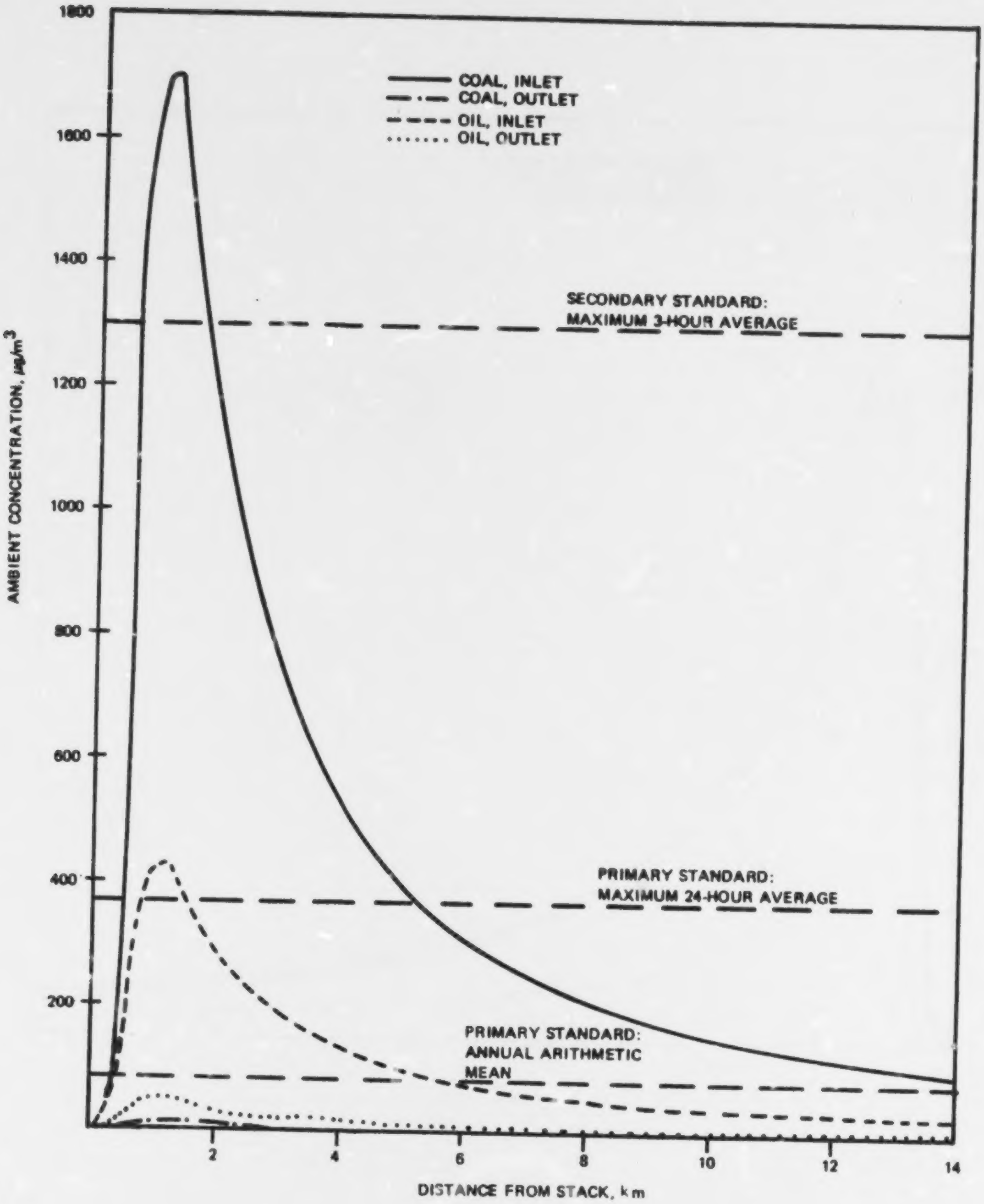

Figure 4-6. Comparison of SO_2 Air Quality Resulting from Coal and Oil Firing under Worst Case Weather Conditions (Tests 201-1 and 202-1)

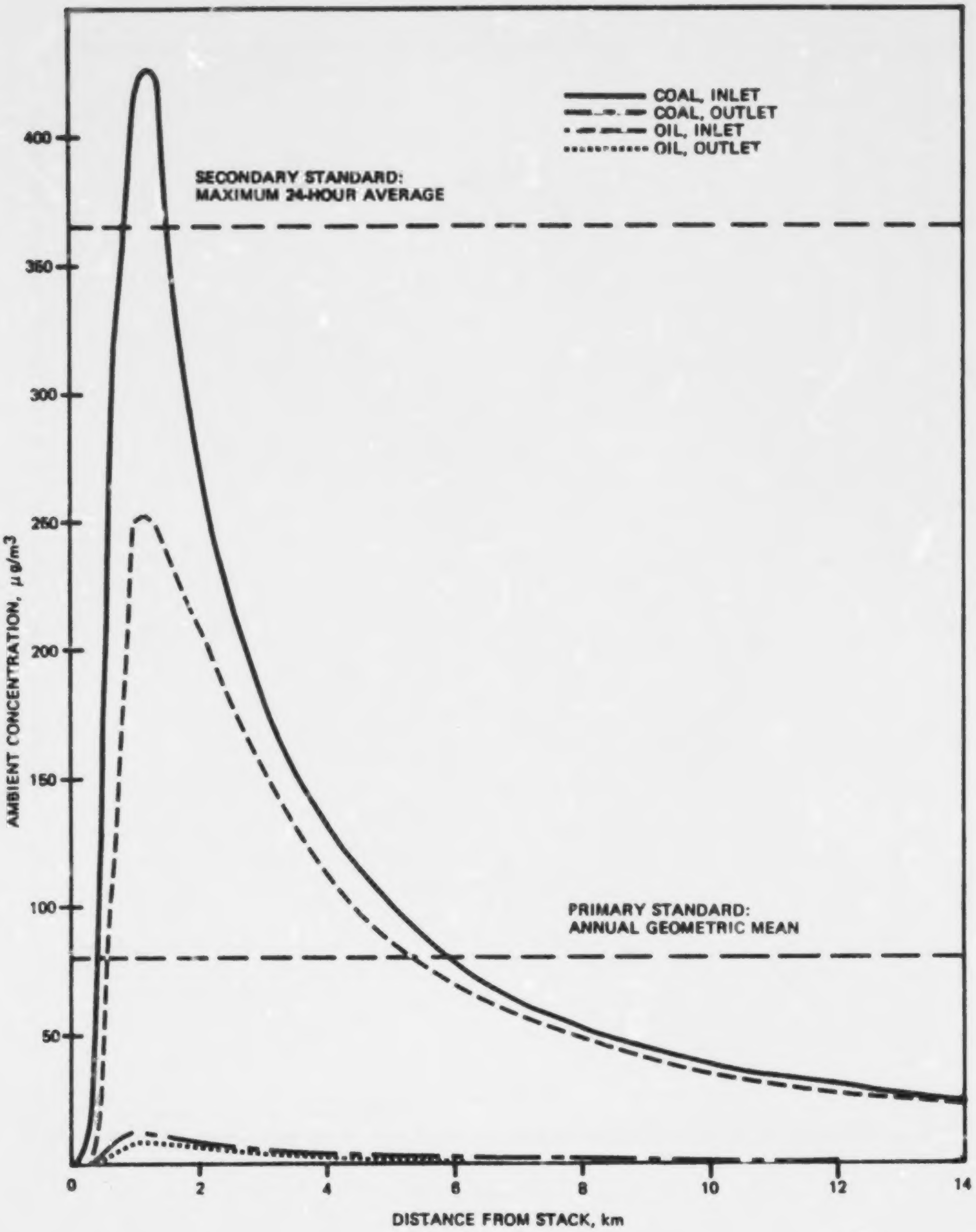

Figure 4-7. Comparison of SO_2 Air Quality Resulting From Coal and Oil Firing Under Typical Weather Conditions (Tests 201-1 and 202-1)

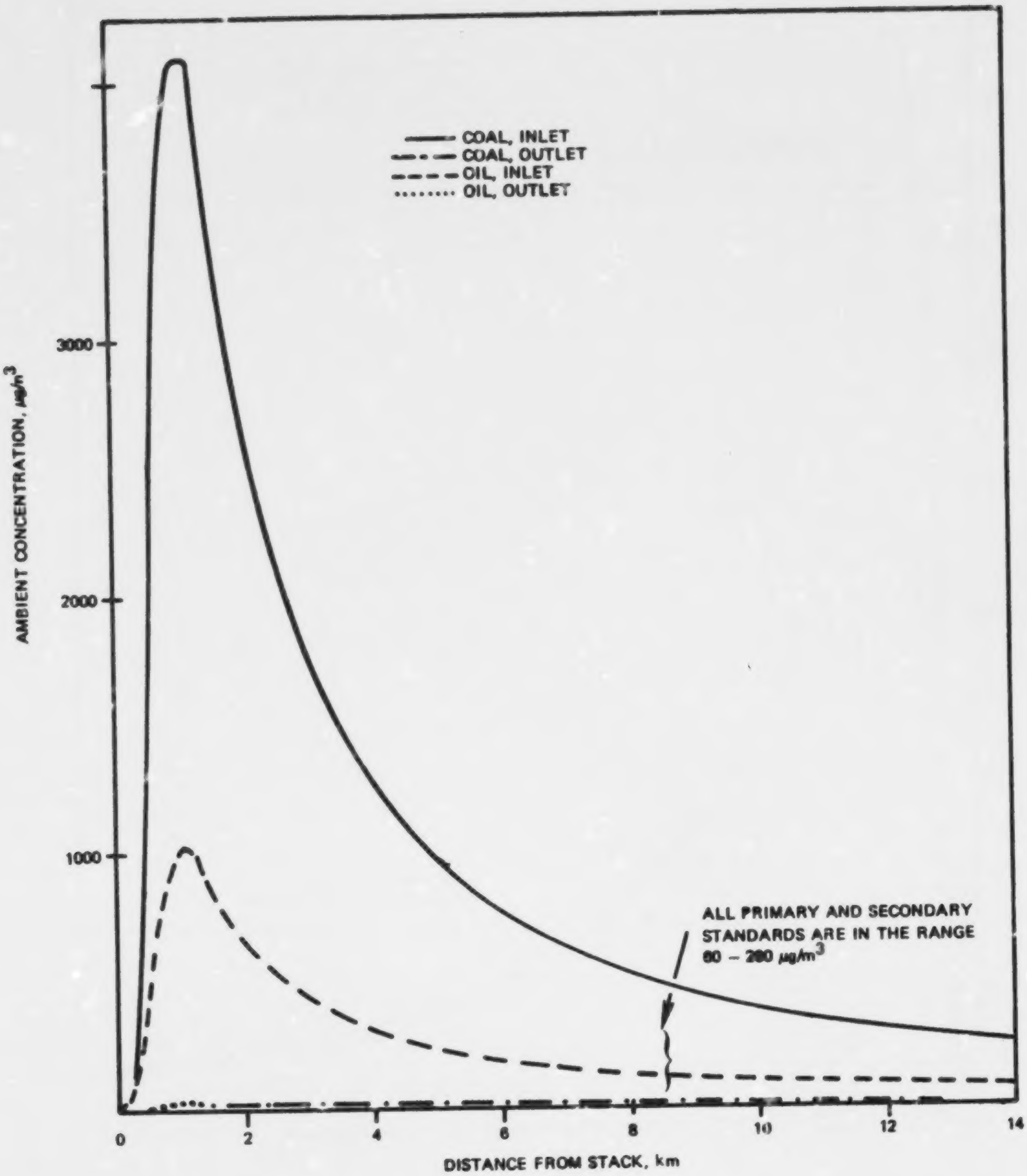

Figure 4-8. Comparison of Particulate Air Quality Resulting from Coal and Oil Firing under Worst Case Weather Conditions (Tests 201-1 and 202-1)

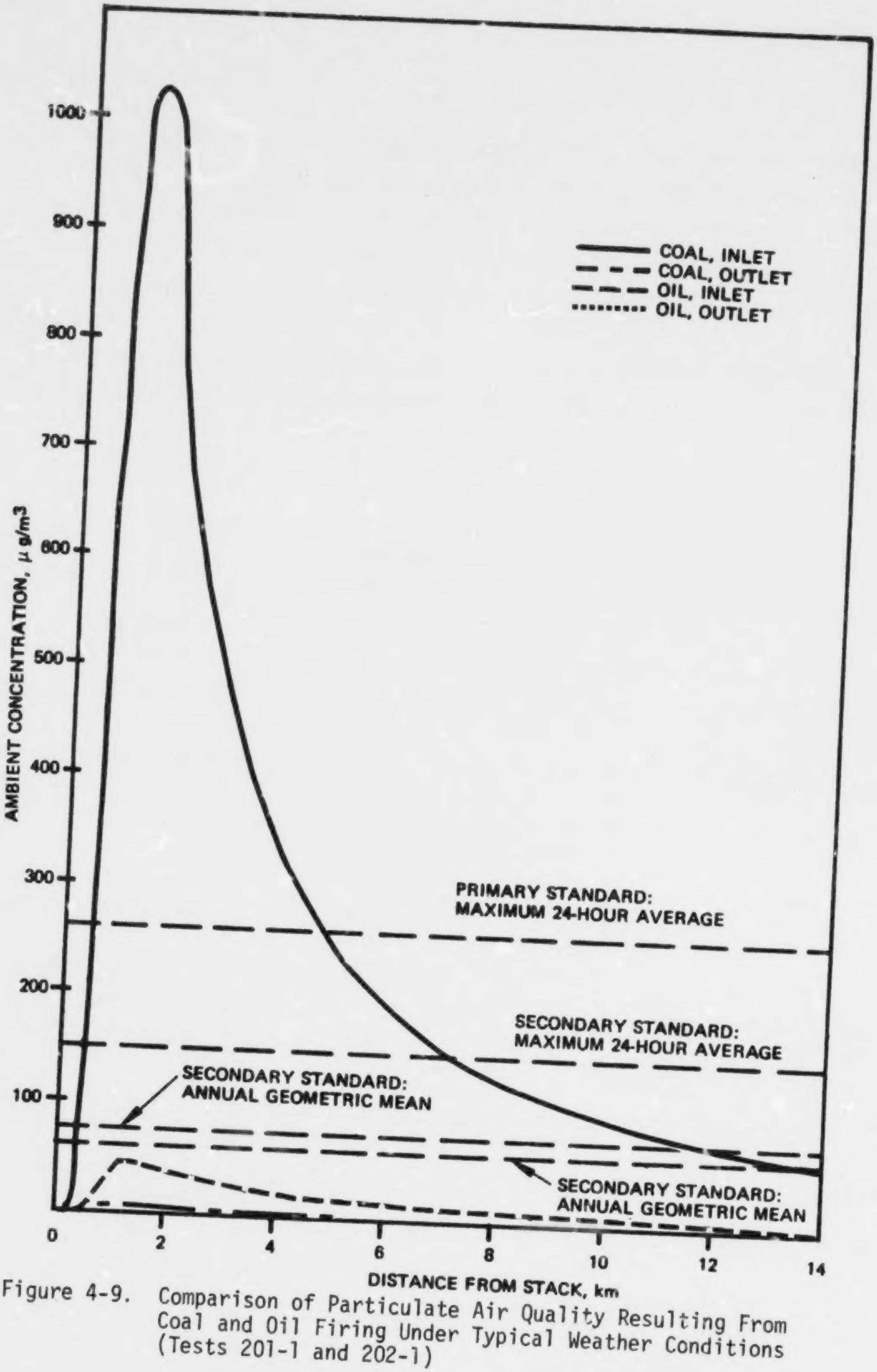

Figure 4-9. Comparison of Particulate Air Quality Resulting From Coal and Oil Firing Under Typical Weather Conditions (Tests 201-1 and 202-1)

arbitrary but realistic set of meteorological conditions. It is implicit in this approach that each set of meteorological conditions remains constant for a sufficient length of time for the ambient air quality to reach steady state conditions at each distance. Note also that the plots represent a single line extending directly downwind from the source.

Table 4-39 presents a summary of the federal ambient air quality standards for each pollutant. The standards were also shown on each plot.

TABLE 4-39. NATIONAL AMBIENT AIR QUALITY STANDARDS FOR CRITERIA POLLUTANTS

Pollutant	Pollutant Standard	
	Primary*	Secondary†
Nitrogen Dioxide	100 $\mu g/m^3$ (0.005 ppm) annual arithmetic mean.	Same as primary
Carbon Monoxide	10 mg/m^3 (9 ppm) maximum 8-hour average; 40 mg/m^3 (35 ppm) maximum 1-hour average.	Same as primary
Sulfur Dioxide	80 $\mu g/m^3$ (0.03 ppm) annual arithmetic mean; 365 $\mu g/m^3$ (0.14 ppm) maximum 24-hour average.	1300 $\mu g/m^3$ (0.05 ppm) maximum 3-hour average
Total Suspended Particulate	75 $\mu g/m^3$ annual geometric mean: 260 $\mu g/m$ maximum 24-hour average.	60 $\mu g/m^3$ annual geometric mean: 150 $\mu g/m^3$ maximum 24-hour average.

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[*] Primary, necessary to protect the public health.

[†] Secondary, necessary to protect the public welfare.

Keeping in mind the caveats mentioned above, several observations can be made:

- The NO_x standard is exceeded under both weather conditions during coal firing. Peak concentrations at 1.2 km from the stack were 3 to 4 times greater during coal firing than during oil firing. During oil firing, the NO_x standard was exceeded under worst case weather conditions but not under typical weather conditions. Since the scrubber does not remove significant amounts of NO_x, there is no substantial difference between the air quality resulting from inlet and outlet emissions. (The boiler has no NO_x controls.)

- CO standards are not exceeded under any conditions. The most restrictive standard is 10 mg/m^3 (10,000 $\mu g/m^3$) and the maximum predicted level is only about 0.2% of this value. As with NO_x there is no substantial difference between the inlet and outlet concentrations. Peak concentrations at 1.2 km from the stack were 3.5 to 4 times greater during coal firing than during oil firing.

- All primary SO_2 standards are exceeded under both weather conditions for uncontrolled emissions from coal firing. Peak uncontrolled SO_2 concentrations were 1.7 times greater during coal firing than during oil firing. Uncontrolled emissions from oil firing exceeded both primary standards under worst case conditions. Under typical conditions only the annual primary standard is exceeded by uncontrolled emissions. For controlled emissions during both coal and oil firing, no standards are exceeded.

- During coal firing, all particulate standards are exceeded under both weather conditions for uncontrolled emissions. Peak concentrations at 1.2 km from the stack were approximately 23 times greater for coal firing than for oil firing. During oil firing, one primary and both secondary standards are exceeded by uncontrolled particulate emissions under worst case weather conditions. No standards are violated under typical weather conditions during oil firing. Controlled emissions for all cases are less than all particulate standards.

CONCLUSIONS

1) Uncontrolled emissions of criteria pollutants produced during coal firing correspond well with emission factors from AP-42. This observation does not generally hold true for oil fired emissions. Full load NO_x emissions from oil firing were 19% lower than the AP-42 emission factor, although they appear to be within the normal range for similar industrial units. CO emissions from oil firing were nearly 63% lower than the AP-42 emission factor. Oil-fired SO_2 and total hydrocarbons correspond well with their respective AP-42 emission factors. Particulate emissions from oil firing, in the absence of coal ash contamination, are approximately twice the value tabulated in AP-42.

2) NO_x emissions increased with increasing load for both coal and oil firing, as expected. Available data indicate that for boiler loadings between 90 and 100%, NO_x emissions from coal firing are approximately three times greater than from oil firing.

3) Observed reductions of NO_x emissions for coal firing and early oil firing tests appear to be due, at least in part, to air leakage into the scrubber outlet sampling line. Data from later oil firing tests, not known to be subject to leakage problems, indicate that NO_x removal across the scrubber is on the order of 2%.

4) Uncontrolled CO emissions from coal firing were 15.9 ng/J (0.04 lb/MM Btu) while those from oil firing were 5.47 ng/J (0.01 lb/MM Btu). This factor of three difference is at variance with AP-42 data indicating that CO emissions from oil firing are 23% lower than those from coal firing. Apparent reductions in CO emissions across the scrubber are not considered significant due to air leakage in the sampling train and the low sensitivity of analysis at the measured CO concentrations.

5) Uncontrolled SO_2 emission rates during coal and oil firing were 1112 ng/J (2.59 lb/MM Btu) and 993 ng/J (2.31 lb/MM Btu), respectively. Removal data indicate an average scrubber removal efficiency of 97% during both coal and oil firing. Controlled SO_2 emissions for coal and oil firing were 36.3 ng/J (0.08 lb/MM Btu) and 26.8 ng/J (0.06 lb/MM Btu), respectively, which are lower than either existing or proposed NSPS limitations.

6) Particulate loadings prior to scrubbing were 2951 ng/J (6.86 lb/MM Btu) during coal firing and 59.0 ng/J (0.14 lb/MM Btu) during oil firing, in the absence of coal ash contamination. Scrubbing removed 99% of the coal fired particulates and 75% of the oil-fired particulates. The lower removal efficiency obtained during oil firing is attributed to the increased fraction of particles smaller than 3 μm; at least 21% of the uncontrolled oil-fired particulates are less than 3 μm in diameter while substantially less than 1% of uncontrolled coal-fired particulates are under 3 μm.

7) There appeared to be a net increase in emission rates across the scrubber for coal fired particulates less than 3 μm in size. This net increase can be attributed to the poor removal efficiency of the scrubber for fine particulates, and to the sodium bisulfate ($NaHSO_4$) and calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) particulates generated by the scrubber. Both $NaHSO_4$ and $CaSO_3 \cdot 1/2\ H_2O$ have been identified at the scrubber outlet but not at the inlet. Although a very slight increase in oil-fired particulates in the 1-3 μm range was observed, a net decrease in particulates less than 3 μm was observed during oil firing. Based on the results of coal firing tests, it appears reasonable that scrubber generated particulates were present in the scrubber outlet stream during oil firing but that the high fine particulate loading associated with oil firing masked detection of these materials.

8) Of the 22 major trace elements analyzed in the flue gas stream during coal firing, 18 exceed their MATE values at the scrubber inlet and 4 at the scrubber outlet. Similarly, for oil firing, 11 exceeded their MATE values at the scrubber inlet while 5 exceeded their MATE values at the scrubber outlet. Elements exceeding their MATE values at the scrubber outlet and which are common to both fuels are arsenic, chromium and nickel. Additionally, iron exceeded its MATE value at the scrubber outlet during coal firing as did cadmium and vanadium during oil firing. The overall removal of trace elements across the scrubber is 99% for coal firing and 87% for oil firing.

9) Polycyclic organic material (POM) was not found in the scrubber inlet or outlet at detection limits of 0.3 $\mu g/m^3$ for either coal or oil firing. MATE values for most POM's are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)pyrene and dibenz(a,h)anthracene - are less than 0.3 $\mu g/m^3$, additional GC/MS analyses at higher sensitivity would be required to conclusively preclude the presence of all POM's at MATE levels.

10) Beryllium emissions after scrubbing were less than or equal to the beryllium MATE value during coal and oil firing. At the measured emission concentrations, the National Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would only be exceeded by boilers of 50 MW capacity for coal firing and 100 MW capacity for oil firing.

11) The combined waste water stream from the boiler operation may not pose an environmental hazard in terms of organic materials since the discharge concentrations of organics are well below their MATE values for both coal and oil firing. The same conclusion may be drawn for inorganic compounds with the exception of cobalt, nickel, copper and cadmium for coal firing and nickel and copper for oil firing since these metals may exceed their MATE values.

12) Organic emissions for coal and oil firing were very similar. Total organic emissions were less than 9 ng/J (0.02 lb/MM Btu) for both tests, and these emissions appear to be primarily C_1 to C_6 hydrocarbons and organics heavier than C_{16}. While uncontrolled emission rates for both coal and oil firing are low, emissions of these organics were further reduced by about 85% in the scrubber unit.

13) The organic compounds identified in the gas samples from both coal and oil firing were generally not representative of combustion-generated organic materials, but were compounds associated with materials used in the sampling equipment and in various analytical procedures. This again confirms the low level of organic emissions.

14) The fraction of fuel sulfur converted to SO_3 during oil firing was 50 to 75% higher than during coal firing. In contrast, the fraction of fuel sulfur converted to sulfates during coal firing was twice that during oil firing.

15) The relatively poor removal efficiency (approximately 30% in both oil and coal-fired tests) for SO_3 across the scrubber is an indication that SO_3 is either present as very fine aerosols in the scrubber inlet, or is converted to very fine aerosols in the flue gas stream as it is rapidly cooled inside the scrubber.

16) Sulfates are more efficiently removed than SO_3 (60% removal for oil firing and 88% for coal firing). This indicates that $SO_4^=$ is probably associated with the larger particulates, which are more efficiently removed than smaller particulates. The higher sulfate removal from the coal flue gases is explained by the higher particulate loading during coal firing.

17) Uncontrolled chloride and fluoride loadings were higher during coal firing (5 and 0.2 ng/J, respectively) than during oil firing (0.2 and 0.02 ng/J, respectively). This was attributed, in the case of chlorides, to a higher fuel chlorine content for coal than for oil. Chlorides were removed with better than 99% efficiency from coal flue gases and with about 51% efficiency from oil flue gases. This difference was attributed to the higher particulate removal efficiency for coal particulates. Fluorides were removed with greater than 86% and about 87% efficiency for coal and oil firing, respectively. Uncontrolled nitrate emissions were 0.08 ng/J during oil firing, and nitrates were removed from oil flue gases with 57% efficiency.

18) Mass closure for most trace elements from coal firing has been found to be in the 75 to 107% range. Mass closure for half of the trace elements from oil-firing is in the 50 to 136% range; closure for the remainder of oil firing trace elements is poorer due to the extremely low elemental concentrations measured and/or contamination of the recycle scrubber solution during coal firing tests.

19) Scrubber cake production during coal firing was 3.3 times greater than during oil firing. Had the multiclone unit been functioning properly, this ratio would be reduced to 2.7, assuming 60% multiclone efficiency. Available data indicate that the principal difference between scrubber cake production rates from coal and oil firing is the particulate loading and associated unbound moisture.

20) The scrubber cake produced during coal firing contained 29% coal fly ash; during oil firing it contained 1% oil fly ash. The trace element concentrations in the coal-fired scrubber cake exceeded their health based MATE values, with the exception of boron. In the oil-fired scrubber cake, all trace elements except antimony, boron, molybdenum and zinc exceeded their health based MATE values. All ecology based MATE values were exceeded by trace element concentrations during both oil and coal firing. Because the trace elements may leach from the disposed scrubber cake, these solid wastes must be disposed of in specially designed landfills.

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SECTION 5

COMPARATIVE ENVIRONMENTAL IMPACT ASSESSMENT

Future energy policies will affect the social, economic, energy, and physical environments. One of the major policy issues involves intensification of coal utilization and the effects of end use of coal relative to fuel oil. It is essential that these effects be determined so that national energy policies involving the alternative energy systems may be developed.

This section evaluates the difference in impacts resulting between emissions from coal and oil combustion in industrial boilers. Absolute impacts resulting from either oil or coal combustion are also analyzed to the extent necessary to evaluate the significance of the differential impacts. The analysis is conducted in five parts. The first part introduces background information pertinent to the development of the environmental assessment, including a review of relevant studies, plant emissions, and air quality forecasts. In the succeeding parts, the major health, ecological, societal, and economic impacts resulting from oil and coal-firing in well-controlled boilers are estimated. The final section assesses the implications of the impacts for energy development by considering: 1) the additional controls which may be needed to mitigate the expected damage levels, and 2) the potential effect of such control needs on energy cost and energy resource development.

INTRODUCTION

Economic and environmental concerns over the nation's energy development policies have precipitated several research efforts to evaluate the consequences of the various energy system alternatives. These efforts deal with all phases of energy development, from fuel production to fuel end use. To organize the various efforts into a systematic, coordinated, environmental assessment structure, the Environmental Protection Agency is implementing a Comprehensive Combustion Environmental Assessment (CCEA) Program. This program has been established for the purpose of integrating together separate data generated by past and current studies into a complete environmental assessment of conventional combustion processes. The integration procedure involves coordination and information exchange between EPA related studies to: 1) determine the extent to which the total environmental, economic, and energy impacts of conventional combustion process can be assessed, 2) identify additional information needed for complete assessment, 3) define the requirements for modifications or additional developments of control technology, and 4) define the requirements for modified or new standards to regulate pollutant emissions. The CCEA Program coordinates and integrates current and future studies encompassing a wide spectrum of environmental assessment areas and conventional combustion processes. Integration of these studies, including the present effort, will provide the basis for energy policies which result in the expanded use of conventional combustion processes at reasonable environmental, economic, and energy costs.

A major research program of particular significance to the industrial combustion assessment activities is the Integrated Technology Assessment (ITA) Program. One current study[12] under the ITA Program will examine growth, impacts, and characteristics of the industrial boiler sector under alternative energy, economic, and environmental policies. This study is to be coordinated under the CCEA Program and will accept the range of data available from CCEA program outputs, including data from the present study. Ultimately, the ITA study will develop an industrial combustion environmental/economic model and combine this with the simulation model of the electric utility system (already under development in a related ITA study) to permit interactive examination of economics and energy policies, and regulations for each combustion sector.

Various studies of the CCEA/ITA Program are relevant to the present study. While there are major uncertainties associated with the findings of the various studies, and many improvements in the analyses are needed before the extent of environmental effects can be determined with certainty, the conclusions and findings are important and the methodologies used in the analyses are valuable tools which are considered and utilized in the present effort. This study contributes to reducing the uncertainties by alleviating two major drawbacks common to previous studies. First, previous studies evaluated the effect of coal combustion on an absolute basis, without comparison to the effects of alternative fuel uses or a "business as usual" fuel use scenario. If coal is to be used instead of other fuels, the real impact of this use is the difference between the effects of the coal use and the other probable alternatives. The present study addresses this issue by developing a comparative environmental assessment between the emissions resulting from coal combustion and the most probable alternative, oil combustion. Second, the previous analyses rely on limited emissions data and numerous assumptions regarding the probable magnitude of the "regulated pollutants" and especially the trace contaminants. The present study avoids the need for these assumptions by generating actual emissions test data for both coal firing and oil firing at a representative industrial boiler site using typical fuels. The tests are plant and fuel specific, and caution should be used in extrapolating study results to the continuum of probable boiler and fuel scenarios.

Plant Emissions

Emissions data from the previous chapters reveal there are significant differences between emissions from controlled oil and coal-fired boilers of 10 MW capacity. Table 5-1 reviews the distinctions for the various pollutant species. Emissions of nitrogen oxides (NO_x) from coal firing are twice the level produced during oil firing. For both oil and coal firing, the total NO_x emission rate exceeds the rates permitted by the New Source Performance Standards (NSPS) for larger utility boilers. However, this is not surprising since the boiler was not equipped with NO_x control equipment. The emissions rates for particulates and sulfur oxides (SO_x) are essentially the same for both oil and coal firing, and the level of these emissions is relatively low considering the level which is permitted by the NSPS for larger utility boilers. The particularly low level of SO_2 emissions (despite the use of high sulfur fuels) observed in tests was due to the high efficiency (greater than 95%) of the flue gas desulfurization system. This system, plus mechanical separators, is also effective in removing particulate matter. Emissions of carbon monoxide (CO) during both oil and coal firing are relatively insignificant, and coal firing produces about two to three times the amount of CO as oil-firing.

Emissions of trace elements (as particulates) during controlled coal firing are not significantly different from that occurring during oil firing (Table 5-1). This occurs despite the fact that, prior to control, combustion flue gases contained appreciably greater concentrations of trace elements than the oil-fired flue gases.

TABLE 5-1 EMISSION RATES FROM A WELL-CONTROLLED OIL- AND COAL-FIRED INDUSTRIAL BOILER

Pollutant	Emissions, gm/sec for 10 MW Boiler[a]	
	Coal Firing[b]	Oil Firing[b]
SO_2	1.10 (15.8)	1.17 (13.1)
NO_x	12.8 (8.8)	6.06 (4.8)
Particulates	.59 (1.4)	.73 (1.6)
CO	.44	.17
As	2.7×10^{-3}	3.2×10^{-4}
Cd	1.2×10^{-5}	7.0×10^{-4}
Co	1.5×10^{-4}	1.3×10^{-4}
Cr	1.6×10^{-3}	1.9×10^{-4}
Cu	2.4×10^{-4}	7.4×10^{-5}
Mo	3.3×10^{-4}	2.6×10^{-4}
Ni	7.7×10^{-4}	2.2×10^{-3}
Pb	2.6×10^{-4}	1.4×10^{-4}
Se	1.2×10^{-3}	6.4×10^{-5}

[a] Data are based on 2 separate tests of nearly equivalent boiler loading (100% capacity during oil burning and 97.5% during coal burning). The composition of the fuels which were used in the test burns is discussed in Chapters 5 and 6.

[b] Figures in parenthesis are emission levels corresponding to new source performance standards for utility boilers to a 10 MW industrial boiler.

Impact on Air Quality

The duration of exposure is important in determining effects of changing air quality. The highest concentrations occur for short periods (usually less than one hour) under meteorological conditions causing plume fumigation. The stack emissions are trapped under an inversion layer, with the plume spreading downward. The frequency of occurrence and the severity of such fumigation conditions varies depending on the site. As a conservative worst case estimate in this study, fumigation conditions were assumed to persist for periods as long as three hours. Typical 24 hour maximum concentrations were estimated assuming Gaussian steady state plume dispersion under conditions of low wind speed and stable atmosphere. Typical 24 hour levels were translated to annual expected concentrations by applying ratios for the one day maximum and annual mean as empirically derived from the Continuous Air Monitoring Project [18,19,20,21]. Effective stack heights were estimated based on assumed meteorological conditions and actual stack parameters measured during the oil and gas-firing tests.

Table 5-2 shows the maximum predicted levels for "criteria pollutants" in the vicinity of an industrial plant. The short term maximum concentrations present the most significant air pollution problem. Of the present ambient air quality standards, the 24 hour NO_x standard appears to be the most difficult for either coal or oil-fired facilities to meet. Coal-firing is more apt to produce violations of the federal ambient standards for NO_x, as the forecasted maximum incremental increase in ambient NO_x from a single plant alone is more than one-half the ceiling level imposed by the NAAQS ceiling value. The next most difficult air quality standards for the coal and oil-fired boiler to meet are short term standards for SO_2 (3 hour average). Coal-firing and oil-firing are estimated to cause maximum increments of 50 and 33 g/m^3, respectively, directly downward of the source. For the case of CO and total suspended particulates, the estimated short term increases from both oil and coal combustion are appreciably less than the ambient standards. For any of the pollutants, it should be noted that the short term maximum concentrations generally occur infrequently (depending on site meteorology) and are usually of very brief duration (usually about 1 hour or less).

TABLE 5-2. COMPARISON OF FEDERAL AIR QUALITY STANDARDS WITH AIR QUALITY PREDICTED TO RESULT FROM OIL AND COAL COMBUSTION IN A 10 MW INDUSTRIAL BOILER

	Maximum Concentration, µg/m^3		
	1-3 Hour[a]	24 Hour[b]	Annual Average[e]
SO$_2$			
Single plant, coal	50	12	3
Single plant, oil	33	8	2
Cluster of plants,[c] coal	225	50	13
Cluster of plants,[c] oil	150	33	8
NAAQS	1300 (3 hrs.)	365	80
PSD Class I increment[d]	25 (3 hrs.)	5	2
PSD Class II increment[d]	700 (3 hrs.)	100	15
Total Suspended Particulates			
Single plant, coal	26	7	2
Single plant, oil	21	5	1
Clustered plants,[c] coal	118	29	7
Clustered plants,[c] oil	95	21	5
NAAQS		260	75
PSD Class I increment[d]		10	5
PSD Class II increment[d]		30	10

TABLE 5.2. (Continued)

NO_x			
Single plant, coal	582	146	39
Single plant, oil	170	43	11
Clustered plants,[c] coal	2640	400	100
Clustered plants,[c] oil	770	180	45
NAAQS		250	100
CO			
Single plant, coal	20	5	1
Single plant, oil	5	1.2	0.3
Clustered plants,[c] coal	400	21	5
Clustered plants,[c] oil	157	5	1
NAAQS	40,000 (1 hr). 1,000 (8 hrs)		

[a] Based on worst case meteorological conditions (plume fumigation).

[b] Based on typical meteorological conditions for 24 hour period.

[c] As a crude means of approximating the effect of an aggregate of plants, the 3 hour and 24 hour levels were adjusted by assuming the additive effect of a plant "cluster." A cluster of plants was assumed to consist of a line of 5 industrial boilers (10 MW each) spaced equally at 200 m apart and aligned with the prevailing wind direction.

[d] Prevention of significant deterioration standards.

[e] The expected annual average levels were estimated based on the conservative end of the range of typical ratios for 24 hour maximum to annual averages as reported in the Air Quality Criteria Documents [18,19,20,21].

For example, Figure 5-1 shows that the short term peak resulting from coal firing would be attained about 1000 m downwind and that ambient concentrations would be diminished to one-half the peak level another 2000 m further downwind. The maximum concentration due to oil firing occurs further downwind (due to a higher plume rise) at about 1200 m from the source, diminishing to one-half this value about 2500 m further downwind.

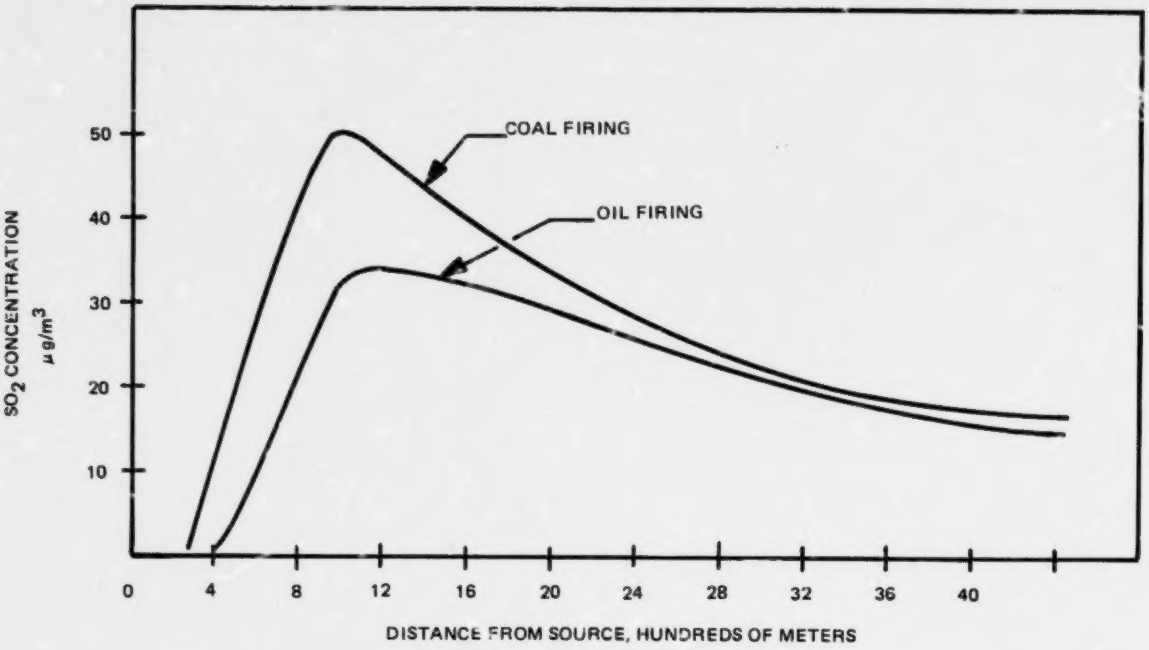


Figure 5-1. Ground level concentration of SO_2 in vicinity of industrial boiler under conditions of plume fumigation.

Federal standards limiting deterioration of air quality are generally more restrictive than the NAAQS, Table 5-2 lists the allowable increment of deterioration for the three classes of growth and development areas. Based on the maximum concentrations of SO_2 and TSP resulting from either coal or oil-firing, industrial boilers would not be permitted in Class I areas (areas meant to be maintained pristine) but might be permitted in

Class II or III areas, depending on the existing air quality. Consequently, siting of the plants would be a major consideration in their environmental acceptability, since areas which already experience marginally acceptable air quality could not tolerate the increases projected to occur. In this respect, it appears that the deterioration standards pose a slightly more difficult attainment problem for coal-fired plants than for oil-fired plants.

Table 5-2 also shows the estimated impact on air quality for a clustered configuration of industrial plants. The estimates are based on the additive result of ambient levels contributed by multiple sources for a siting scenario in which five 10 MW industrial boilers are spaced 200 meters apart in a line. The scenario is by no means the most adverse case probable for an industrial setting. Many industrial zones may contain a greater concentration of sources, and sources of greater magnitude as well. However, the siting scenario of the four clustered plants illustrates the potentially high short term concentrations which may occur when well-controlled oil or coal-fired industrial boilers are sited closely together, and underscores the necessity for careful siting of sources to avoid potential violations of the NAAQS and Significant Deterioration Amendments.

Fuel selection exerts a significant role in the environmental acceptability of the clustered array of plants. Table 5-2 shows that short term ambient levels of NO_x in the vicinity of the cluster will violate the NAAQS when boilers are coal-fired but will meet standards when oil is burned. This finding applies to a boiler operating without NO_x control. Burning of coal also produces concentrations of CO four times that estimated for oil burning, however, the magnitude of the CO levels are inconsequential with respect to the NAAQS. Coal-burning produces only slightly higher levels of TSP and SO_2 than oil-burning.

COMPARATIVE HEALTH IMPACT

The health effects of exposure to high concentrations of the various pollutants are well known and have been tabulated throughout the literature, [4]. However, the specific extent to which health is affected by ambient pollutant exposure levels (dose response relationships) is unclear. Moreover, it is unclear how pollutant specific dose response curves may be related to the over all health effects of the gas-aerosol complex associated with fossil fuel combustion products.

Most attempts to establish dose response functions for ambient pollution levels involve the formulation of some indicator which is then assumed to represent the entire spectrum of primary and secondary pollutants present. The indicator (usually sulfur dioxide, total particulates, or sulfates) is then related to mortality or morbidity data for various areas by various statistical approaches designed to factor out effects of other variables (e.g., population age, climatology, etc.). Dose-response curves derived from these studies are then employed to estimate health effects of air quality changes resulting from proposed projects.

Recently the health effects model by Lundy and Grahn[5] has been developed for application in the National Coal Utilization Assessment Studies being conducted at Argonne National Laboratories. The model combines mortality functions for suspended sulfates as developed by Morris and Novak[6] and age-dependent and established response curves for cigarette smoke. The mortality dose-response functions for suspended sulfates are based on statistical studies of various populations experiencing different sulfate exposures. Unlike the dose-response air pollution studies, investigations of smokers have been relatively well controlled with respect to age, degree of exposure, and effect. Thus, to expand the predictability of the sulfate dose-response curves to populations of different age distribution (e.g., future populations), the cigarette response curves are adjusted to fit the observed mortality/sulfate data, resulting in a model which predicts age-specific death rates. This elaboration is important because death rates vary exponentially with age, and shifts in the age distribution of a population will result in substantial shifts in total mortality. Accordingly, the Lundy Grahn Model utilizes projections of the population age distribution to estimate the age-specific and total death rates due to air pollution at any specific time in the future. The basic relationship of the model is:

$$B(X, Xo) = \frac{ae^{bX}}{1 + c\ e^{-d(X-Xo)}}\ S$$

where B is the number of excess deaths per year for the population of age X which was exposed to the sulfate concentration S (in $\mu g/m^3$) since age Xo. The constants a,b,c and d are coefficients to fit the model to cigarette smoking mortality data and response data for a specific population subgroup exposed to air pollution.

The Lundy Grahn Model is being used in the ongoing National Coal Utilization Assessment program to estimate excess mortality resulting from increased coal utilization. Air diffusion modeling was conducted first to predict a population-weighted exposure increase for suspended sulfates. The Lagrangian Statistical Trajectory Model of Argonne National Laboratory[10] which assumes a constant transformation of SO_2 to sulfate, is employed in the estimation procedure. Then, based on the predicted exposure increase and projections of the population age distribution, excess death rates are calculated for each age and summed to yield the expected mortality associated with coal combustion. Table 5-3 shows the estimated effects of an average exposure increment of 8.95 $\mu g/m^3$ suspended sulfates predicted to result from coal-firing of power plants throughout the Central United States. (The degree of power plant coal firing is assumed to increase in the region from the current level of 178 million tons per year to 820 million tons per year in 2020). The projected levels of power plant coal utilization are predicted to cause significant health effects in future years. These forecasts may be adjusted to approximate the additional health impact which can be expected to result from coal combustion in industrial boilers. The results of Table 5-3 are adjusted to reflect: 1) the emissions rate for coal-fired industrial boilers relative to power plant boilers, and 2) the relative amount of industrial boiler coal use relative to utility consumption.

TABLE 5-3. EFFECTS OF COAL COMBUSTION IN POWER PLANTS IN CENTRAL U.S. [7]

Year	Increase in Death Rate, Number of deaths/Million persons/Year	Reduction In Expectation of Life At Birth[a]
1985	28-130	17 - 79 days
2000	181-809	136 days - 1.7 years
2020	150-665	160 days - 1.8 years

a. The range of values represents the expected and upper 80% confidence limit given by Morris and Novak.[6] The effects are calculated corresponding to an expected average exposure increment of 8.95 $\mu g/m^3$ suspended sulfates.

Figure 5-2 presents the adjusted projections for the industrial boiler scenario. No distinction is necessary between oil and coal firing, since the emission rates for SO_2 were found to be essentially the same (see Table 5-2). The lower emissions rate from industrial boilers accounts for suspended sulfate levels appreciably less than those projected for the utilities. It is noted that the adjustments for industrial effects in Figure 5-2 do not include an adjustment for the spatial aspect of population exposure. Because the industrial boilers are typically located in more urban areas than power plants, the population-weighted exposures under-

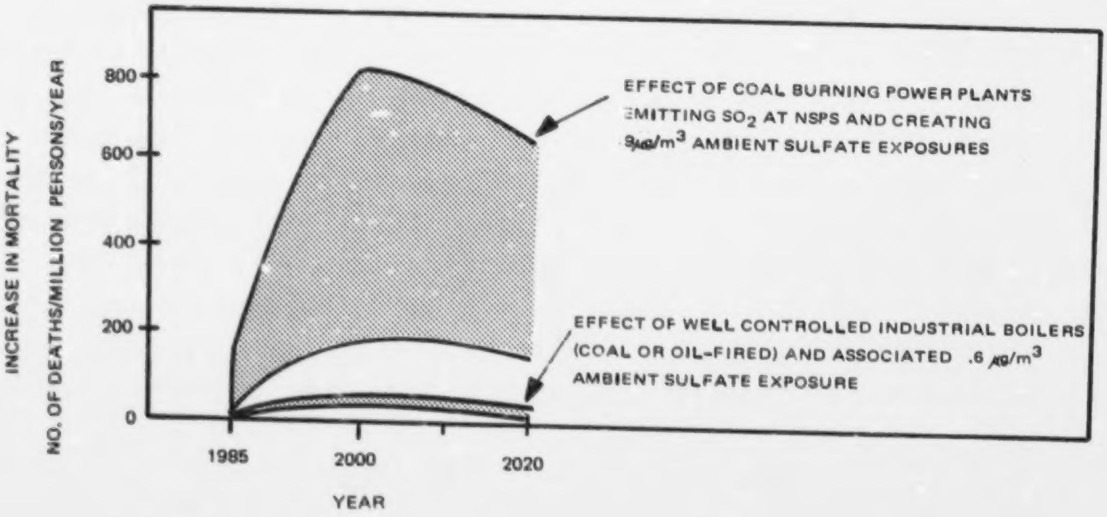


Figure 5-2. Effects of coal or oil combustion in well controlled industrial boilers. The range of values represent the expected and upper 80% confidence limit given by Morris and Novak[6].

a. Based on assumption that 60% of all industrial fuel use is for steam generation (boilers), and that the amount of industrial fossil fuel use is 1.4 times that of the utilities,[9]. Additionally, for purposes of worst case impact consideration, it is assumed that 100% of the industrial boilers may use or be converted to-burn coal.

b. The emissions of sulfur dioxide from an industrial well-controlled coal-fired plant and an NSPS conforming coal-fired power plant of the Midwest Coal Utilization Study are .09 $lb/10^6$ Btu and 1.2 $lb/10^6$ Btu, respectively.

lying the estimates of Figure 5-2 are understated for the industrial situation. However, the understatement is probably minor, since the formation and transport of airborne sulfates is a long range and region wide problem, and effects of localized sulfate formation from the source are generally minimal. It is also noted that the comparisons are applicable to the specific fuels and boiler types, and caution is advised in extrapolating the results to fuels of different compositions.

Figure 5-2 shows that the expected health effects caused by air pollution (as indexed by suspended sulfates) from oil or coal-firing of well-controlled industrial boilers are minimal compared to the effects which might result from utility boilers emitting SO_2 at the rate prescribed by the NSPS, and substantially less than that which would be expected under current industrial boiler controls. The maximum impact is expected to occur in the year 2000, when the proportion of population in the highest risk age groups will be greatest. For each million persons, the number of increased deaths expected to occur annually due to well-controlled industrial boilers is 12 to 55 in the year 2000. Based on the tests of the present study, and the sulfate health effects model, there is no indication that the difference in mortality rates resulting from well-controlled coal-firing and well-controlled oil-firing would be significant. The test data and the sulfate mortality model also indicate that relative mortality effects would not be significantly different between uncontrolled coal and uncontrolled oil firing. (See Volume II.) However, the absolute levels for expected mortality rates due to uncontrolled coal or oil combustion would be roughly 30 times greater than that expected from well-controlled combustion.

Health effects caused by sulfate levels may also be expressed in terms of morbidity. Table 5-4 presents data for increases in incidents of health disorders due to ambient sulfate exposures. In those areas which already experience high sulfate levels, respiratory diseases may increase significantly with slight increases of suspended sulfates due to industrial boiler emissions. For example, in areas where the threshold level 10 $\mu g/m^3$ is exceeded regularly, the increase of .6 $\mu g/m^3$ of sulfate concentration associated with well controlled industrial boilers would be estimated to pro-

TABLE 5-4. HEALTH IMPACTS OF SULFATE AEROSOL[11]

Pollutant and Health Effect	Population at Risk	Assumed Baseline Frequency of Disorder within Population at Risk	Pollutant Concentration Threshold For Effect	Effect Increase as % of Baseline Per Pollutant Unit Above Threshold
Sulfates				
Mortality	Total Population	Daily death rate of 2.58 per 100,000	25 $\mu g/m^3$ for one day or more	2.5% per 10 $\mu g/m^3$
Aggravation of Heart and Lung Disease in Elderly	Same as above for oxidants function	Same	9 $\mu g/m^3$ for one day or more	14.1% per 10 $\mu g/m^3$
Aggravation of Asthma	Same as above for oxidants function	Same	6 $\mu g/m^3$ for one day or more	33.5% per 10 $\mu g/m^3$
Lower Respiratory Disease in Children	Same as above for nitrogen dioxide function	Same	13 $\mu g/m^3$ for several years	76.9% per 10 $\mu g/m^3$
Chronic Respiratory Disease				
Nonsmokers	62 percent of population age 21 or older	Two percent prevalence	10 $\mu g/m^3$ for several years	134% per 10 $\mu g/m^3$
Smokers	38 percent of population age 21 or older	Ten percent prevalence	15 $\mu g/m^3$ for several years	73.8% per 10 $\mu g/m^3$

duce an 8% increase in the incidence of chronic respiratory disease caused at the threshold level. Once again, adverse effects are no more likely to occur by oil-firing than by coal-firing in the well-controlled boiler.

In addition to potential health effects created by long range sulfate levels from industrial boilers, high concentrations of pollutants in the range of the industrial complex pose a potentially serious health problem. The Lundy-Grahn model may also be applied to estimate mortality effects caused by ambient levels of SO_2 and total suspended particulates. The model gives the following relationships when fitted to Lave and Seskin dose response data[12] for SO_2 and TSP:

$$\text{per } 10^6 \text{ males: } \quad \frac{.823\, e^{.064X}}{1 + 100\, e^{.12(X-Xo)}} \quad (.835\ TSP + .715\ SO_2)$$

$$\text{per } 10^6 \text{ females: } \quad \frac{.056\, e^{.088X}}{1 + 100\, e^{-.2(X-Xo)}} \quad (.835\ TSP + .715\ SO_2)$$

If the model is applied to typical concentrations expected to occur in the vicinity of a clustered array of industrial sources, the expected increase in mortality is appreciable. (See Table 5-2.) Figure 5-3 illustrates the estimated impact on mortality. For example, when boilers are coal-fired, populations of the age 50 are predicted to experience increases in death rates of 306 male and 200 female deaths per million persons per year. When boilers are fired with oil, the increased death rate is about one-third less that experienced under ambient exposures from coal-firing. The difference is attributable primarily to the higher plume rise of the oil-fired boiler emissions which lends to greater dispersion and lower ambient concentrations of SO_2 and TSP in the vicinity of the sources. The absolute impact of both the well-controlled oil-fired and coal-fired boilers is relatively minor when compared to the anticipated impact of either current industrial boiler emissions or even those emissions levels corresponding to the NSPS. (See Figure 5-2.) It is reminded that the NSPS for utility boilers permit an SO_2 emissions rate twelve times greater than the emission rate measured for the reference well-controlled coal-fired boiler, and eight times greater than the emissions for the reference oil-fired boiler. Emissions at the rate associated with the NSPS would yield average ambient

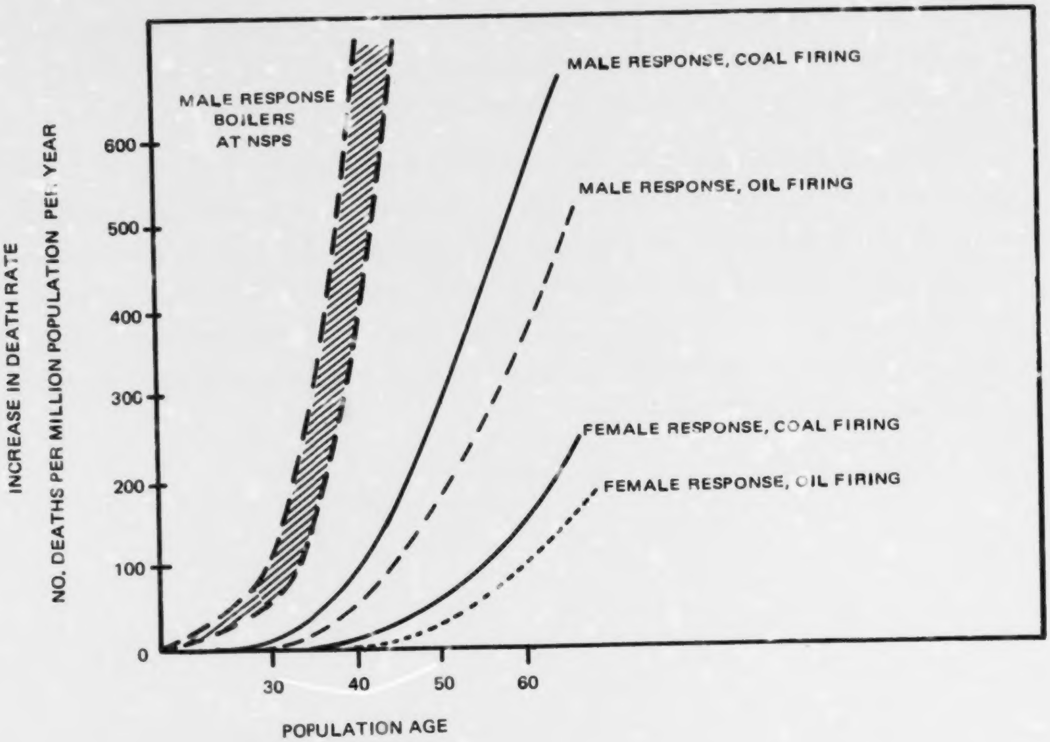


Figure 5-3. Increase in mortality rates in vicinity* of clustered industrial boilers.

*Based on the ambient air quality forecasts, the sphere of effect is assumed to extend several km outside the clustered array of plants. (See Volume III). The increased mortality rates are based on the maximum annual average concentration of TSP and SO_2 expected in the vicinity of the industrial plant cluster.

annual SO_2 levels between 60 and 160 $\mu g/m^3$, jeopardizing the primary standard of 80 $\mu g/m^3$.

Effect of Trace Elements--

Trace elements from coal combustion emissions enter the atmosphere and are then dispersed to the upper atmosphere or deposited in the environment around the sources. The principal routes of entry to man are by inhalation, drinking water and food.

Table 5-5 summarizes the annual average atmospheric concentrations of various elements expected in the vicinity of a single well-controlled coal or oil-fired industrial boiler of 10 MW capacity. The estimates are based

TABLE 5-5. EXPECTED TRACE ELEMENT CONCENTRATIONS IN VICINITY OF A 10 MW CONTROLLED INDUSTRIAL BOILER

Element	Annual Ambient Concentration, g/m^3		Typical Urban Air Concentration[a] $\mu g/m^3$	Allowable Exposure Level[b] $\mu g/m^3$
	Coal-Firing	Oil-Firing		
As	7.7×10^{-3}	5.7×10^{-4}	1×10^{-2}	50
Cd	3.4×10^{-5}	1.3×10^{-3}	3×10^{-1}	20
Co	4.2×10^{-4}	2.3×10^{-4}	2×10^{-4}	10
Cr	4.5×10^{-3}	3.4×10^{-4}	1×10^{-2}	50
Cu	6.8×10^{-4}	1.3×10^{-4}	5×10^{-2}	100
Mo	9.4×10^{-4}	4.6×10^{-4}	1×10^{-1}	500
Ni	2.2×10^{-3}	3.9×10^{-3}	1.4	100
Pb	7.3×10^{-4}	2.5×10^{-4}	2.4	20
Se	3.4×10^{-3}	1.1×10^{-4}	2×10^{-4}	20

[a] Based on data reported in Reference 22.

[b] Based on ambient air objectives proposed for hazardous waste management facilities,[23].

on the assumption that trace elements exhibit the same relationships as described earlier for estimation of total suspended particulates. Also included in Table 5-5 is a listing of concentrations considered acceptable for continuous ambient exposure. The allowable concentrations are based on proposed regulations for control of air pollution from hazardous waste management facilities, as required by Section 3004 of the Resource Conservation and Recovery Act. It is clear that the air concentrations of elements resulting from operation of the industrial boiler are several orders of magnitude (4 to 6) below the "allowable exposure level." Moreover, the predicted maximum concentrations are also substantially below typical urban ambient background levels with the exception of selenium and cobalt concentrations which approach or slightly exceed the endogenous levels. Considering the error bound of a factor of three associated with the trace element analyses of this project, it is concluded there is only a slight difference between the expected ambient levels of trace elements from either coal or oil-firing with the possible exception of cadmium. Ambient cadmium levels from oil-firing are about 40 times greater than that caused by coal-firing.

Clustering of plants or increases in amounts of trace elements in fuels could increase the expected concentrations of trace elements by an order of magnitude. However, even with such an increase, the concentration of most elements listed in Table 5-5 would be an order of magnitude less than typical urban maximum concentrations, and the concentration of all elements would still be several orders of magnitude less than the "allowable exposure level."

A primary concern in emissions of trace elements is the contribution of these elements to body burden due to exposure to water and food. To estimate this contribution, pollutant deposition rates are approximated by the product of the ambient concentrations and the deposition velocity of the pollutant. The deposition rate is dependent on particle size. Table 4-10 (Vol. II) shows that particles emitted from the controlled oil and coal-fired industrial boiler of this study are predominantly three microns or less in diameter. The deposition velocity of particles this size over grass surfaces is approximately 0.1 to 0.2 cm/sec,[13]. Accordingly, the deposition rates of the various trace elements were approximated and are shown in Table 5-6.

The significance of the deposition rates is evaluated by considering the associated effect on drinking water and diet. The pathway to drinking water is by run-off of soil particles containing deposits of trace elements, and the pathway to the diet is by plant uptake from trace elements in the soil. In either pathway, the incremental concentration of elements in the soil determines the extent of the potential impact. Table 5-7 summarizes the maximum predicted soil concentration in the vicinity of the scenario of five clustered industrial boilers of 10 MW each. The concentrations are estimated by assuming mixing of the deposited elements to a depth of 10 cm, and over a period of 40 years. For the majority of the trace elements, only minor increases over the background soil levels would be expected. However, the concentration of a few elements may increase significantly. It is predicted that coal firing will cause a 60% increase in the selenium

TABLE 5-6. ANNUAL DEPOSITION OF TRACE ELEMENRS IN VICINITY[b] OF CONTROLLED INDUSTRIAL PLANTS

Element	Annual Deposition Rate,[a] g/m^2-yr			
	Coal Firing		Oil Firing	
	Single Plant	Cluster	Single Plant	Cluster
As	2.4×10^{-4}	1.0×10^{-3}	1.9×10^{-5}	7.8×10^{-5}
Cd	1.1×10^{-6}	4.5×10^{-6}	4.1×10^{-5}	1.7×10^{-4}
Co	1.3×10^{-5}	5.3×10^{-5}	7.2×10^{-6}	3.0×10^{-5}
Cr	1.4×10^{-4}	5.8×10^{-4}	1.1×10^{-5}	4.5×10^{-5}
Cu	2.1×10^{-5}	8.6×10^{-5}	4.1×10^{-6}	1.7×10^{-5}
Mo	3.0×10^{-5}	1.2×10^{-4}	1.5×10^{-5}	6.2×10^{-5}
Ni	6.9×10^{-5}	2.8×10^{-4}	1.2×10^{-4}	4.9×10^{-4}
Pb	2.3×10^{-5}	9.5×10^{-5}	7.9×10^{-6}	3.3×10^{-5}
Se	1.1×10^{-4}	4.5×10^{-4}	3.5×10^{-6}	1.4×10^{-5}

[a] Calculated by assuming a particle deposition velocity of 0.2 cm/sec. The deposition velocity is multiplied by the annual average concentration to estimate the total deposition rate.

[b] The deposition rate is calculated for the location where the maximum average annual concentration occurs.

TABLE 5-7. LONG TERM EFFECT OF EMISSIONS FROM CLUSTER OF CONTROLLED INDUSTRIAL BOILERS ON SOIL CONCENTRATIONS OF TRACE ELEMENTS

Element	Increased Soil Concentration After 40 years,[a] µg/g		Typical Soil Concentration[b] µg/g	Increase Over Average Soil Concentrations, %	
	Coal	Oil		Coal	Oil
As	2.7×10^{-1}	2.1×10^{-2}	6.0	4.5	.35
Cd	1.2×10^{-3}	4.5×10^{-2}	.06	2.0	70
Co	1.4×10^{-2}	8.0×10^{-3}	8	.2	.10
Cr	1.5×10^{-1}	1.2×10^{-2}	40	.4	.03
Cu	2.3×10^{-2}	4.5×10^{-3}	20	.1	.02
Mo	3.2×10^{-1}	1.7×10^{-2}	2	16	.80
Ni	7.5×10^{-2}	1.3×10^{-1}	40	.2	.4
Pb	2.5×10^{-2}	8.8×10^{-3}	10	.3	.08
Se	1.2×10^{-1}	3.7×10^{-3}	.2	60	1.8

[a] Based on deposition rate (Table 5-6), an assumed mixing depth of 10 cm and soil density of 1.5 g/cm^3.

[b] Based on data compiled in Reference 3.

soil concentration and a 16% increase in molybdenum levels. Oil-firing is apt to cause less impact on trace element soil levels, but is predicted to cause a 70% increase in cadmium concentrations. The significance of the elevated soil concentrations is evaluated by considering the associated increase in trace element concentration in plant tissues and drinking water.

The concentration of elements in plant tissues is related to the biologically available fraction of the elements in the soil. This is often expressed as the soluble concentration in the soil, and is some fraction of the total endogenous concentration reported in Table 5-7. Plants possess the ability to concentrate elements from dilute soil solutions. This ability is dependent on the concentration of elements in the soil, and usually increases with decreasing soil concentration. The ratio of concentration of elements in plants to the concentration in the soil is known as the concentration ratio. Table 5-8 lists average plant concentration ratios for various elements. The data are based on various published data as complied in a study by Battelle,[3]. The effect of increased trace element soil loadings (caused by 40 years of boiler cluster emissions) on concentration of the elements in plants is then estimated by assuming that the soluble portion of the loadings are available for plant takeup (Table 5-8). The estimates reveal that seven of the nine elements show incremental burden in plants amounting to one half to 1/700 the typical plant concentration levels. Thus, for these seven elements, the increase in plant concentration would appear to be insignificant in terms of effect on human health by route of the food chain, or in terms of actual plant life itself. For most elements, coal-firing appears to exert a slightly greater impact on trace element plant burden, however, this differential effect may be considered nearly insignificant in view of the uncertainities associated with chemical analyses employed to determine stack emissions rates. The elements predicted to produce the most notable burdens in plant tissue are cadmium and molybdenum. Oil firing is predicted to result in plant concentrations of cadmium an order of magnitude greater than the endogenous levels, and coal-firing is expected to produce a thirty-fold increase in typical molybdenum concentrations.

Cadmium is considered highly toxic to plants and animals. Mammals tend to absorb cadmium continually, accumulating high body levels which

TABLE 5-8. LONG TERM EFFECT OF EMISSIONS FROM CLUSTER OF CONTROLLED BOILERS ON CONCENTRATIONS OF ELEMENTS IN PLANTS

Element	Concentration Ratios[a]	Solubility Of Elements[a] %	Typical Concentration in plants,[a] μg/g	Increase in Concentration of plants,[b] μg/g Coal	Oil
As	4.2	9	.08 - .55	.1	.008
Cd	222	40	.04 - .50	.1	4.0
Co	87	.4	.05 - .25	.005	.003
Cr	250	.004	.23	.001	.0001
Cu	1000	.1	14	.02	.005
Mo	900	9	.9	26	1.4
Ni	331	.1	3	.03	.04
Pb	2	—	2.7	.05	.02
Se	4	21	.2	.1	.003

[a] Extracted from Reference 3.

[b] Calculated by multiplying concentration ratio by the incremental increase in soil concentration (Table 105) by the concentration ratio by the fraction of the element which is soluble.

adversely affect the respiratory, cardiovascular, nervous, and reproductive systems, disrupt kidney and liver functions, and cause intestinal disorders. Cadmium levels as low as 15 μg/g in plants may cause injury to man.[24] Cadmium levels in some areas are believed to be approaching threshold levels, and it is believed that cadmium concentrations in cigarettes might cause smokers to exceed thresholds of observable symptoms of cadmium poisoning if exposed to additional sources of cadmium,[25]. Consequently, the addition of cadmium to the environment in significant quantities is a serious concern. However, it should be noted that present day levels of cadmium emissions from non-controlled industrial boilers are substantially greater than those well-controlled levels discussed here.

In contrast to cadmium, molybdenum is considered to exhibit a low order of toxicity. Molybdenum has been found to be a necessary trace element in the body for the proper functioning of flavoprotein enzymes.[26]

Still, incidents of animal injury have been reported in the vicinity of steel plants where livestock were observed to develop inflammation of bowels and degenerative changes in liver cells. The injury was associated with high molybdenum levels in the cows' blood.[27] The threshold diet levels for animals or man are unclear. The incident of cow injury was caused by grazing in a pasture containing 20 to 100 μg/g of Mo. It should also be noted that the occupational air exposure threshold for molybdenum is two orders of magnitude greater than that for cadmium, and the potable water standard for Mo is 40 times greater than the cadmium standard.

The actual impact of trace element emissions on plant burden depends greatly on many site-specific variables, such as temperature, precipitation, soil type, water chemistry, and plant species at a given site. Of major concern are the endogenous concentrations of elements in soil, water, and the atmosphere. Where trace element concentrations are approaching threshold limits, emissions from industrial plants will exert a greater influence on health impacts. This consideration is particularly relevant with respect to environmental buildup of cadmium because high background levels of this element already exist in many areas. The impact on trace element burdens in plants from controlled boilers, whether oil or coal-fired, may be significantly less than that from existing boiler control. Based on the present study, the major difference between trace element buildup from oil versus coal firing of well-controlled boilers is the higher cadmium levels associated with oil burning.

Trace elements also enter the plant via foliar absorption. Intake from the leaf surface to the interior occurs through stomatal openings, walls of epidemal cells, and leaf hairs. Although relatively little is known regarding the efficiency of foliar intake, it would appear that the plant burden produced by soils containing long term deposits is several orders of magnitude greater than that which could be transferred from foliar interception of trace elements in the atmosphere. Soil concentrations are the result of accumulation of elements over the long-term, and crops raised in these soils tend to concentrate the trace elements in the plant tissue. By contrast, the foliar intake rate can be no greater than the deposition rate on the plant surface, and there is much uncertainty regarding the efficiency of the plant in absorbing the deposited particles.

Thus, it is clear that the soil uptake scenario (Table 5-8) represents the more adverse case for plant uptake of trace elements. This scenario assumes no interference (e.g., animal or crop uptake) with trace element buildup in soils over a 40 year period, and a fixed concentration of elements in the soil despite crop uptake.

Trace element emissions also affect the quality of drinking water. The impact of trace element particle deposition on runoff water concentration will be related to the relative increase in soil concentration due to long term atmospheric deposition of elements. The actual runoff concentrations may be estimated by applying average sediment burden rates for representative runoff per unit of watershed area. The sediment is assumed to carry the cumulative deposits of metals orginating from the boiler emissions. Table 5-9 summarizes estimates of increased soluble metals concentrations for runoff waters in the vicinity of a cluster of industrial plants. The estimated concentrations are three to seven orders of magnitude less than the standards for livestock drinking water and potable water. Two elements, selenium and molybdenum, are predicted to exceed background concentrations for metals in runoff waters after 40 years of coal-firing in the plant cluster. The concentration of metals in runoff waters due to oil firing is predicted to be slightly less than that occuring from coal firing; in either case, hazard to human health by drinking water is remote.

IMPACT ON ECOLOGY

The ecological environment will be affected by air emissions and by solid waste residuals generated by air pollution control equipment. Operation of the controlled industrial boilers is not expected to produce significant water pollution problems, since wastewaters produced are generally acceptable to the municipal water treatment systems.

Effect of Air Emissions

A major ecological impact category most likely to be affected by industrial boiler emissions is plant life. Of the major gaseous pollutants emitted by fossil fuel combustion, plant life is most affected by SO_2 and NO_x in the concentration ranges expected. Concentrations of CO and hydrocarbons produced by a single industrial boiler or a clustered arrangement of boilers are considered to cause negligible impact on vegetation.[21,28]

TABLE 5-9. TRACE ELEMENT CONCENTRATION IN RUNOFF WATER IN VICINITY OF CLUSTERED CONTROLLED INDUSTRIAL BOILERS

Element	Typical Background Concentration of Soluble Metals In Runoff Water[a] µg/ml	Increase In Soluble Metals Concentration In Soil After 40 years[b] µg/ml		Increase In Soluble Metals Concentration In Runoff Water[c] After 40 years µg/ml		EPA Proposed Maximum Acceptable Concentration For Livestock µg/ml	Standard As Critical Concentration In Potable Water µg/ml
		Coal	Oil	Coal	Oil		
As	4×10^{-4}	2.4×10^{-2}	1.9×10^{-3}	2.4×10^{-5}	1.9×10^{-6}	2×10^{-1}	1×10^{-2}
Cd	1×10^{-4}	$.5 \times 10^{-3}$	1.8×10^{-2}	$.5 \times 10^{-6}$	1.8×10^{-5}	5×10^{-2}	1×10^{-2}
Co	3×10^{-5}	$.6 \times 10^{-4}$	3.2×10^{-5}	$.6 \times 10^{-7}$	3.2×10^{-8}	1	5×10^{-2}
Cr	1×10^{-5}	$.6 \times 10^{-5}$	$.5 \times 10^{-6}$	$.6 \times 10^{-8}$	$.5 \times 10^{-9}$	1	2×10^{-2}
Cu	2×10^{-5}	2.3×10^{-5}	4.5×10^{-6}	2.3×10^{-8}	4.5×10^{-9}	5×10^{-1}	1×10^{-2}
Mo	1×10^{-6}	2.9×10^{-2}	1.5×10^{-3}	2.9×10^{-5}	1.5×10^{-6}	—	5×10^{-1}
Ni	1×10^{-4}	7.5×10^{-5}	1.3×10^{-4}	7.5×10^{-8}	1.3×10^{-7}	—	5×10^{-2}
Pb	7×10^{-4}	2.5×10^{-2}	8.8×10^{-3}	2.5×10^{-5}	8.8×10^{-6}	1×10^{-1}	1×10^{-2}
Se	8×10^{-5}	$.2 \times 10^{-1}$	$.7 \times 10^{-3}$	$.2 \times 10^{-4}$	$.7 \times 10^{-6}$	5×10^{-2}	1×10^{-2}

[a] Based on average soil particle runoff rate of 1000 µg/ml of runoff water, and soluble endogenous concentration of metals in soils.[3]

[b] Based on increase in trace element concentration (Table 5-7) and solubility of elements (Table 5-8).

[c] Based on average soil particle runoff rate of 1000 µg/ml of runoff water, and increased soluble metals concentration in soil after 40 years.

The levels of NO_x and SO_2 expected to occur in the vicinity of industrial boilers approaches the threshold injury values for these pollutants. Only very sensitive plants in the vicinity of a cluster of industrial boilers are likely to suffer injury, and such injury would be limited to a downwind sector and a range of about 2 km length beginning a few hundred meters from the perimeter of the cluster.

While neither hydrocarbon or nitrogen oxides would be expected to cause plant injury at the ambient doses predicted near the boilers, the secondary pollutants (ozone and peroxyacylnitrates) formed by reaction of these pollutants are considerably more toxic. The formation of secondary compounds in boiler stack plumes and the impact of the boiler nitrogen oxides emissions on urban photochemical smog depend on complex relationshops which are not yet totally understood. Therefore, it is not possible to reliably estimate the effect of NO_x emissions levels to photochemical compounds. However, based on typical regional emissions figures, it appears that emissions from industrial fuel combustion provide a significant source of the regional emissions of NO_x necessary for photochemical smog. Approximately 20% of the nation's NO_x emissions are produced by industrial fuel combustion,[29].

If NO_x emissions from industrial boilers are a significant contributor to photochemical smog, then there is valid concern that boiler emissions may contribute to plant injury. Coal-firing presents the greatest concern. NO_x emissions from coal-firing of the boiler of the present study were measured to be twice the magnitude produced during oil-burning. The boiler is not equipped with NO_x control. The effects of photochemical air pollution on plant life have been observed frequently at various different severities throughout the United States. In addition, the effect of the major constituents of photochemical smog (products of nitrogen oxides and organic compounds) on plants has been investigated separately. The pigmentation of small areas of palisade cells is characteristic of ozone injury, and a bronzing of the undersurface of leaves is typical for peroxyacyenitrate injury. Table 5-10 illustrates the relatively low levels of ozone which will produce significant plant injury to crops. The concentrations shown are typical of many areas experiencing photochemical air pollution, and suggest the necessity for concern over sources emitting high levels of NO_x.

TABLE 5-10. PROJECTED OZONE CONCENTRATIONS WHICH WILL PRODUCE, FOR SHORT-TERM EXPOSURES, 20 PERCENT INJURY TO ECONOMICALLY IMPORTANT VEGETATION GROWN UNDER SENSITIVE CONDITIONS,[30]

Concentrations producing injury in three types of plants, ppm			
Time, Hr	Sensitive	Intermediate	Resistant
0.2	0.40-0.90	0.80-1.10	1.00 and up
0.5	0.20-0.40	0.35-0.70	0.60 and up
1.0	0.15-0.30	0.25-0.55	0.50 and up
2.0	0.10-0.25	0.20-0.45	0.40 and up
4.0	0.07-0.20	0.15-0.40	0.35 and up
8.0	0.05-0.15	0.10-0.35	0.30 and up

Nitrogen oxides may also cause injury to vegetation by direct contact. The significant oxides of nitrogen are NO and NO_2. The major oxide in combustion emissions is NO. However, after residence in the atmosphere, NO is converted to NO_2 by photolysis and by photochemical interaction with hydrocarbons. The effect of NO_2 on plant life has been studied under controlled laboratory conditions. Acute injury is characterized by collapse of cells and subsequent development of necrotic patterns. Chronic injury, caused by exposure to low concentrations over long periods, is characterized by chlorotic or other pigmented patterns in leaf tissue. Such injury results in reduction of growth and reproduction. Only limited data are available to characterize the effect of NO on plants. Generally, it appears that NO leads to effects somewhat similar to those observed for NO_2, but at slightly higher threshold concentrations. Therefore, for worst case evaluations of the impact of ambient NO_x levels, it is assumed that NO_x exists as NO_2, and that the NO_x levels are not depleted by the photochemical reactions which typically occur in urban areas.

Figure 5-5 illustrates the threshold concentrations at which various degrees of damage result from exposure to NO_2. Based on the expected concentration of NO_x in the vicinity of the coal-fired industrial plant cluster, and the assumption it is converted entirely to NO_2, it appears that acute leaf damage may be anticipated to occur as a result of short term plume fumigations, and that chronic effects (including growth and yield reductions)

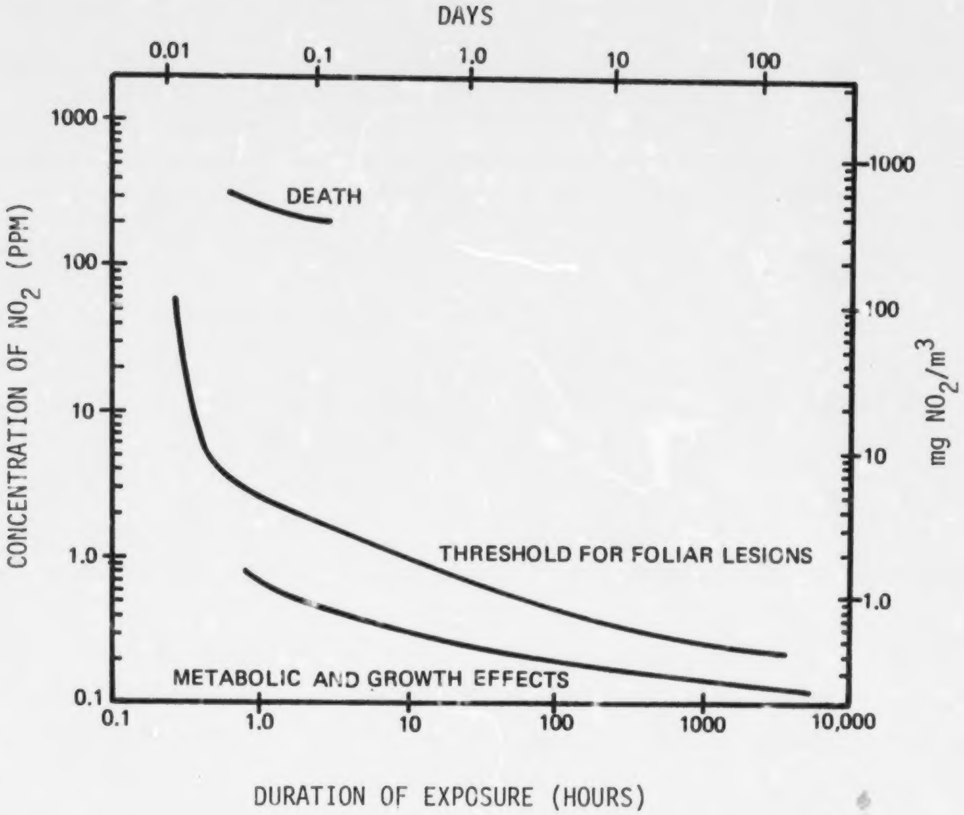


Figure 5-5. NO_2 threshold concentrations for various degrees of plant injury ,[31].

may be noticed over the long term. The extent of the damages would be localized within a one or two km range from the plant cluster, and would be expected to occur to those plants most sensitive to NO_2 injury (e.g., cotton, navel orange, spinach, etc.). However, NO_2 injury to plants from oil firing is not as likely to occur. Maximum short term ambient concentrations of NO_x near the plant cluster are estimated to be about one third that resulting from coal-firing, or below the threshold levels which induce plant injury. (See Figure 5-5.)

Acute (short term) injury to vegetation by SO_2 exposure is characterized by damaged leaf areas which first appear as water soaked spots, and later appear as bleached white areas or darkened reddish areas. Chronic SO_2 injury is usually characterized by chlorosis (yellowing) which develops from lower concentrations over extended periods of time. Either acute or chronic SO_2 injury may result in death or reduced yield of the plant if the extent of the damaged tissue exceeds 5 to 30 percent of the total amount of foliage.

The impact of the expected SO_2 concentrations varies with the plant species. Threshold injury in sensitive plants may be caused by short-term SO_2 levels as low as 30 $\mu g/m^3$,[17]. Table 5-11 summarizes the broad categories of sensitivity for different plants. Grain, vegetable, pasture, and forage crops are susceptible to SO_2 damage for most of the growing season. These crops may suffer yield reductions in areas where industrial boilers have been sited together in clusters. However, the damage would be highly localized, and the extent of the most severe injury would probably result in only minor yield losses. Figure 5-6 shows that peak SO_2 concentrations expected to occur near the clustered network of controlled industrial plants will probably cause only traces of leaf damage to occur in the more sensitive plant species. However, certain adverse combinations of frequent fumigations and boiler sitings could result in crop damage of significant extent. If ambient levels of SO_2 are approaching plant damage thresholds in the vicinity of the industrial boilers, the potential effect of the type of fuel utilized could be significant. Based on the boiler tested in the present study, and the dose-response relationships of Figure 5-7, it appears that once ambient SO_2 levels are equivalent to leaf destruction thresholds, coal-firing would result in total leaf destruction rates significantly higher than that produced by oil firing.

It should be noted that the plant damage thresholds illustrated by Figure 5-6 apply to conditions of temperature, humidity, soil moisture, light intensity, nutrient supply, and plant age which cause maximum susceptibility to injury. The occurrence of such conditions are rare. In fact, in the unlikely event that all such conditions are met, the dose-response curves indicate that plant injury could occur without a violation of the federal air quality standard for the 3 hour or 24 hour concentration

TABLE 5-11. SENSITIVITY OF COMMON PLANTS TO SO_2 INJURY,[2]

Vegetation			Crops		
Sensitive	Intermediate	Resistant	Sensitive	Intermediate	Resistant
White pine	Maple	Sugar maple	Alfalfa	Irish Potato	Corn
Goldenrod	Virginia creeper	Phlox	Barley	Clover	Sorghum
Cottonwood	White oak	Oak	Oats	Sweet clover	
Virginia creeper	Elm	Maple	Rye		
Aster	Shortleaf pine	Shrubby willow	Wheat		
Gooseberry	Aster		Sweet potato		
Elm	Linden		Soybean		
Wild grape			Sweet clover		
American elm			Cotton Tobacco		
White ash			Clover		
Virginia pine					
Tulip tree					

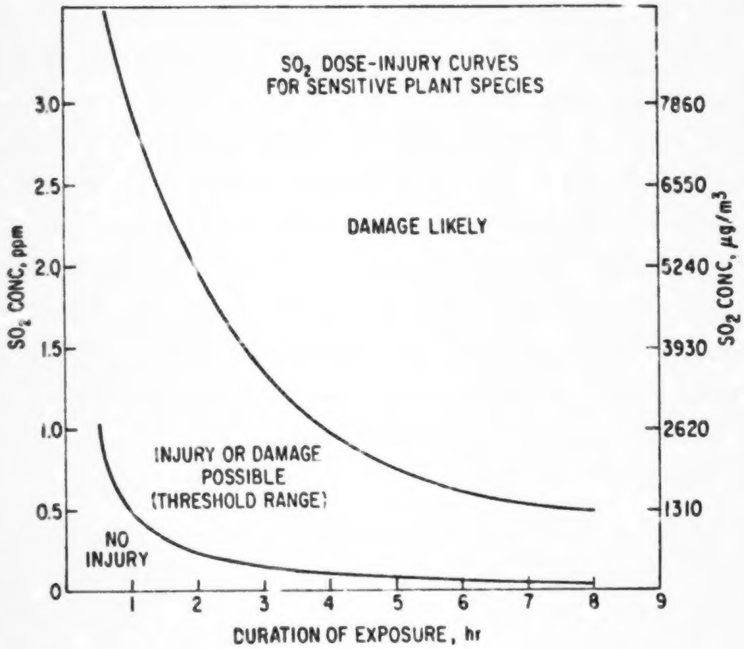


Figure 5-6. SO_2 Dose-Injury Curves for Sensitive Plant Species,[17].

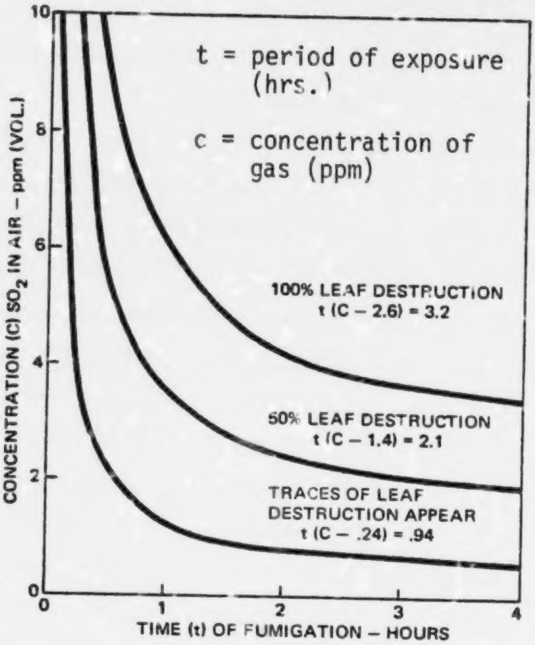


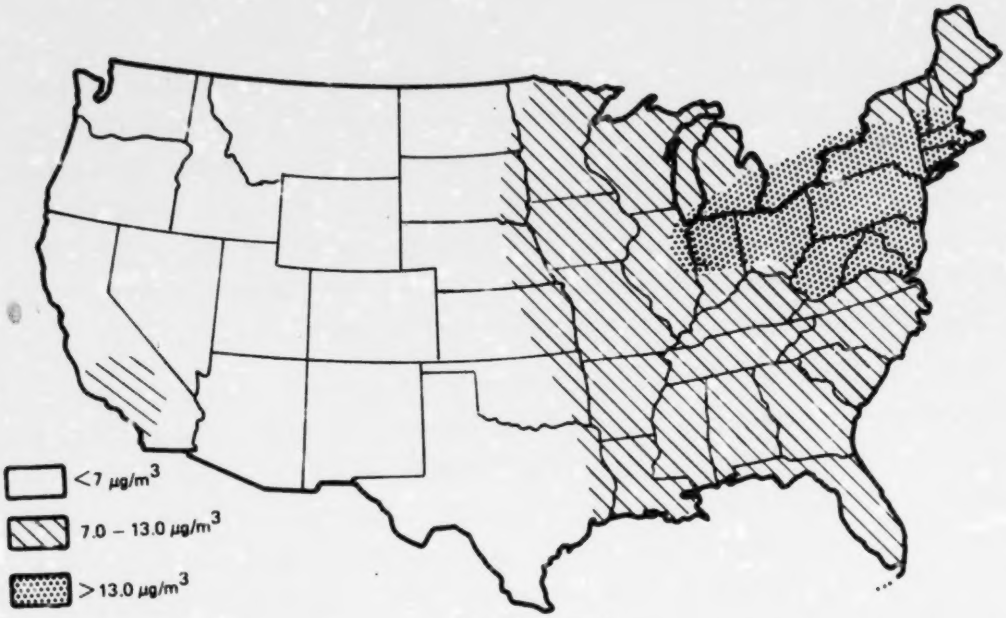
Figure 5-7. Dose-Response curves for Alfalfa exposed to SO_2 under conditions of maximum absorption,[18].

of SO_2. Additional susceptibility may also result from synergistic effects of sulfur dioxide and other pollutants. Particularly relevant to the urban environment are combinations of sulfur dioxide and ozone. Moderate to severe injury of tobacco plants have been observed for four hour exposures to concentrations of 0.1 ppm (262 $\mu g/m^3$) SO_2 in combination with 0.03 ppm ozone. Because high ozone levels are a frequent problem in the vicinity of urban areas, susceptibility to plant injury by SO_2 pollution is probably greater in those areas where industrial boilers are typically sited. One of the major concerns associated with fossil fuel utilization is acid precipitation resulting from wet deposition of suspended sulfur and nitrate compounds. Data show that there has been an intensification of acidity in the northeastern region of the U.S. since the mid 1950's. Precipitation in a large portion of the eastern U.S. averages between pH 4.0 and 4.2 annually. Values between pH 2.1 and 3.6 have been measured for individual storms at distances several hundred miles downwind of industrial centers. The areas experiencing highest acidity are typically downwind of the areas where sulfur emissions are highest,[25], [31].

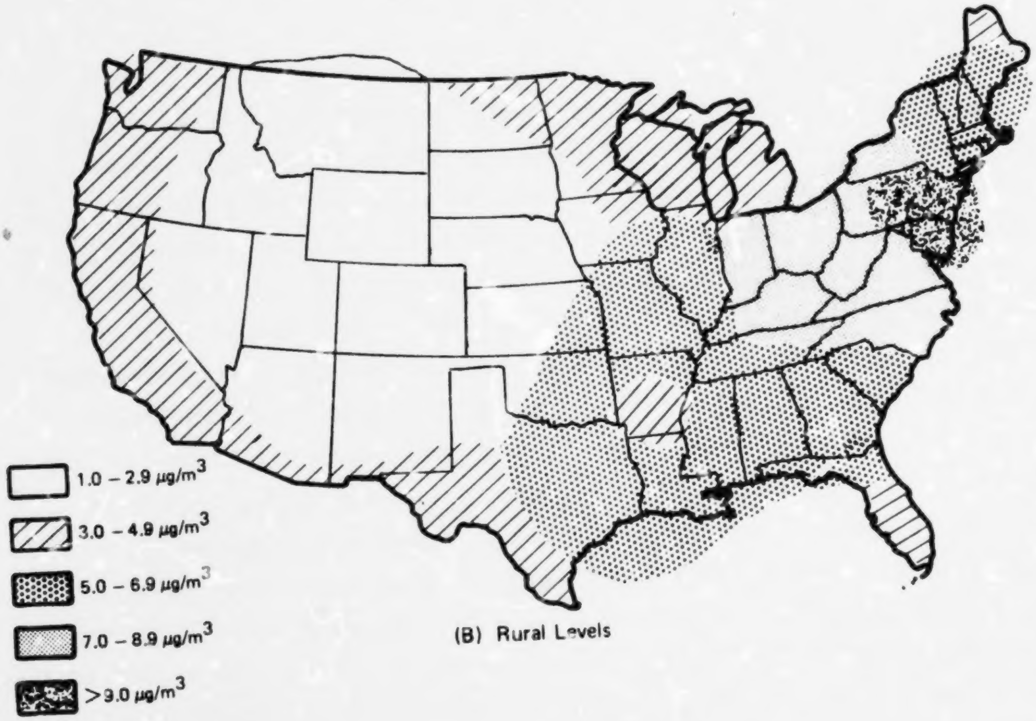
Acid rain affects plant life in varying degrees depending on the pH and the type of plant species. Experiments show that the effects on plants may include reduction in growth or yield, leaf damage, death, and chlorosis. Acid rain also has been shown to affect aquatic organisms, and it is believed that thousands of lakes are now experiencing reductions in fish population due to acidification between pH 5.0 and 6.0,[31].

The impact of fossil fuel combustion in controlled industrial boilers boilers on acid precipitation and plant damage is relatively minor. Based on stack tests as the reference boilers, the resulting levels of sulfates would be essentially the same whether the controlled boilers are coal fired or oil fired. In the previous discussion, it was estimated that controlled industrial boilers would account for a level of .6 $\mu g/m^3$ suspended sulfate in the central region of the U.S. This level is substantially below ambient sulfate concentrations associated with areas experiencing significant acid precipitation. Typical ambient sulfate levels prevalent in the U.S. are shown in Figure 5-8. However, it should be noted that the NSPS for utility boilers permit a greater sulfur oxides emission rate than that rate which was measured from the controlled industrial boiler. Thus, typical (non-controlled) industrial boilers burning coal or oil and emitting at rates equivalent or higher than that of the NSPS would cause suspended sulfate levels an order of magnitude higher than that resulting from controlled boilers.

Plants may also sustain injury from elevated levels of trace elements. As shown previously (Table 5-8), trace element concentrations in vegetation near clustered industrial boilers would not be expected to exceed levels observed to be toxic in plants. However, under conditions which would cause the most adverse 40 year accumulations of trace elements in soils around the emission sources, it is possible that both molybdenum and cadmium could be concentrated in vegetation at levels causing plant injury. The effects of cadmium toxicity in plants are wilting, chlorosis, necrosis, and reduction of growth. Substantial declines in yield of the soybean, wheat and lettuce have been observed when the tissue concentration of cadmium in foliar parts of these species was as low as 7, 3 and 11.5 $\mu g/g$ respectively. Molybdenum is considered to be one of the least toxic of


< 7 μg/m3
7.0 – 13.0 μg/m3
> 13.0 μg/m3

(A) Urban Levels


1.0 – 2.9 μg/m3
3.0 – 4.9 μg/m3
5.0 – 6.9 μg/m3
7.0 – 8.9 μg/m3
> 9.0 μg/m3

(B) Rural Levels

Figure 5-8. Geographical distribution of typical sulfate levels in the United States ,[2].

trace elements. However, it is concentrated heavily by the uptake system of most plants, and it is estimated it may be present in concentrations up to 26 μg/g (i.e., 30 times the maximum background level) in the foliar tissue of plants near an industrial boiler cluster. It is not clear if this Mo level is destructive to vegetation, but dietary concentrations as low as 5 μg/g have been known to cause diarrhea in cows, and Mo levels from 20-100 μg/g in grazing pastures have resulted in death of cows,[32].

Based on tests of the reference industrial boiler, it appears that emissions from oil firing will result in potentially high cadmium plant burdens while coal firing is more apt to cause elevated levels of molybdenum. While the evaluation is based on most adverse potential conditions, it does illustrate the need to consider fuel use, as well as other site specific issues (e.g., magnitude and location of sources, stack heights, background levels of trace elements), in planning for adequate protection of vegetation and agriculture near industrial boiler plants.

Effect of Solid Wastes

A major environmental concern involving the use of fossil fuels is the generation of coal ash and flue gas desulfurization (FGD) sludges. The quantity of such wastes depends on the proportion of coal utilization and the amount of SO_2 removed from stack gases. It has been estimated that by 1985 coal ash will be generated at a rate of 92 x 10^6 tons/year and FGD sludges at a rate of 33 x 10^6 tons/year (dry basis). Landfill is the common means of disposal for these wastes. By 1980 it is estimated that 0.4 to 0.7 acres of land per MW of boiler capacity will be required for disposal purposes,[36]. The composition of the wastes will depend on the fuel source, the boiler design, and the flue gas desulfurization system. Most FGD processes generate a waste sludge consisting predominantly of calcium sulfite and sulfate. Various trace elements are also found in the FGD sludge. The trace elements originate from reagents used in SO_x removal, from process water, from trace elements in the combusted coal or oil, and from fly ash (noncombusted portion of coal) which is collected by the FGD scrubber system. Fly ash and bottom ash usually consist of about 80 percent silica, alumina, iron oxide, and lime. The composition of trace elements found in bottom and fly ash is similar.

Table 5-12 shows the quantities of coal ash and FGD sludge collected during operation of the reference 10 MW industrial boiler studied in this project. Coal-firing of this controlled boiler produces approximately three times more scrubber cake than oil firing produces; this is due to the higher rate of particulate matter generated by coal combustion and the subsequent collection of the particulate matter by the FGD scrubber system. The quantities of bottom ash and fly ash generated by oil burning is relatively insignificant. A portion of the fly ash generated by coal burning is collected with the scrubber cake of the FGD system, while most of the fly ash is recovered by cyclone collectors upstream of the scrubber. Bottom ash generated by coal firing represents a significant waste disposal problem, and is generally managed in conjunction with the scrubber cake wastes.

Based on the test results of scrubber cake produced by the reference boiler, it appears that coal firing produces a greater enrichment of trace elements in the scrubber cake. Table 5-13 shows that only four elements exhibited higher concentrations in the scrubber cake produced by oil firing. However, either scrubber cake contains sufficient amounts of heavy metals and toxic substance to pose difficult waste disposal problems.

TABLE 5-12. GENERATION RATE OF SOLID WASTE FROM 10 MW CONTROLLED INDUSTRIAL BOILER

	Rate of Production, kg/hr.	
Waste	Coal Firing	Oil Firing
Bottom ash	80	1
Fly ash	240[a]	2[a]
Scrubber cake	1100	400

[a] This is amount of fly ash recovered by cyclone collector. Approximately 25% of the fly ash is recovered in scrubber and removed with scrubber cake.

TABLE 5-13. COMPOSITION OF FGD SCRUBBER CAKE

Element	Concentration, μg/g Coal Firing	Concentration, μg/g Oil Firing	Relative Concentrations, Coal/Oil
Ca	60715	192030	.3
Mg	1458	1776	.8
Sb	315	122	2.6
As	532	135	3.9
B	857	2405	.4
Cd	13	7	1.9
Cr	141	33	4.3
Co	424	231	1.8
Cu	112	35	3.2
Fe	47241	3867	12.2
Pb	297	104	2.9
Mn	51	15	3.4
Mo	1117	666	1.7
Ni	114	148	.8
V	195	161	1.2
Zn	282	19	14.9
Se	256	128	2.0
Sr	642	163	3.9
Al	45310	4625	9.8
Zr	106	39	2.7

FGD scrubber wastes and coal ash are usually disposed in impoundment ponds or landfills. The major concern in either disposal approach is the release of trace elements to ecosystems in localized areas surrounding the disposal sites. Lateral and upward movement of trace elements through the soil to plant rooting zones may be possible, and contamination of ground and surface waters may occur. Additional adverse consequences include the diversion of land from other uses, and aesthetic degradation at the disposal site.

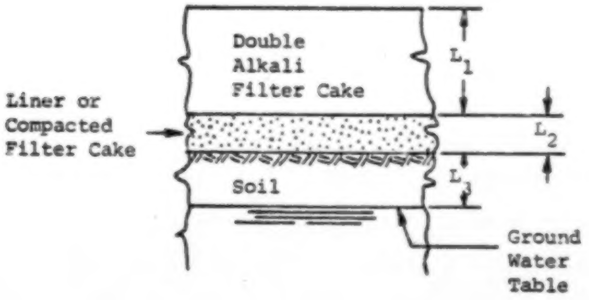
Because of the limited experience concerning land disposal of wastes, and the long time lags preceding future potential adverse impacts, there is significant uncertainty regarding the level of restrictiveness necessary to assure the environmental adequacy of various land disposal methods. Because of such uncertainty, it seems likely that stringent waste disposal regulations will be proposed to stabilize waste sludges, preventing their migration in the terrestrial environment and the movement of leachate to underground water sources.

Disposal of FGD sludges and coal ash is already subject to regulations at the state level. Recent federal legislation (the Resource Conservation and Recovery Act) now requires that criteria be developed to classify wastes and suitable disposal management techniques. Under the proposed criteria, due in fall of 1978, it is plausible that FGD sludges and coal ash may be classified as hazardous waste, and that disposal of these wastes will be restricted by the stringent requirements now being proposed for hazardous waste management facilities. Typically, these requirements would restrict the land disposal of hazardous wastes to "secure landfills" designed to provide protection for all-time of the quality of ground and surface waters. By definition, the secure landfill would prevent significant adverse impact to certain environmental sectors (i.e., public health and ecology). Unfortunately, the secure landfill, is, by definition, an ideal design which cannot be attained except at very great cost. There is, therefore, a need to define reasonably attainable land disposal designs which offer a high level of environmental protection.

Various recent efforts have been conducted to define appropriate landfill criteria. In one pertinent study,[16] the effectiveness of three scenario landfill designs for the disposal of FGD scrubber cake were evaluated. The scrubber cake considered is that generated by the Double Alkali FGD system utilized at the reference industrial boiler of this study. Migration of leachate to the groundwater and the loading rate of dissolved solids into the groundwater were estimated by considering the permeability of the landfill layers and the solubility of solids as determined from laboratory tests. Table 5-14 summarizes the analysis of the three landfill cases. As indicated, permeability of the soils and the scrubber waste is the primary factor in initiating leachate migration.

TABLE 5-14. LEACHING RATES FOR THREE LANDFILL DESIGNS

Case	L_1 (feet)	L_2 (feet)	L_3 (feet)	K_1 (cm/sec)	K_2 (cm/sec)	K_3 (cm/sec)	K_{eff} (cm/sec)	t_1 (years)	t_2 (years)	Q_s (lb/ft^2/yr)
I	18	2	10	10^{-5}	10^{-6}	10^{-4}	7.7×10^{-6}	1	20	1.04
II	18	2	10	10^{-5}	10^{-6}	10^{-8}	1.5×10^{-8}	200	6000	0.0033
III	20	1	10	10^{-5}	10^{-9}	10^{-4}	3.0×10^{-8}	100	3000	0.0066


Double
Alkali
Filter Cake
L_1
Liner or
Compacted
Filter Cake
L_2
Soil
L_3
Ground
Water
Table

L_1 = Depth of uncompacted filter cake (feet)

L_2 = Depth of compacted filter cake or liner (Case III) (feet)

L_3 = Depth of soil (feet)

K_1, K_2, K_3 = Coefficients of permeability of layers 1, 2, and 3, respectively (cm/sec)

K_{eff} = Effective permeability of overall filter cake plus soil layers (cm/sec)

t_1 = Time for migration of leachate to groundwater table (years)

t_2 = Time for washout of major dissolved solids from filter cake (years)

Q_s = Loading rate of total dissolved solids to groundwater (lb/ft^2/yr)

In the first case, all net precipitation becomes leachate, and the time to reach groundwater is about one year while the time to wash out the major portion of the soluble solids is about 20 years. The overall washout rate of soluble solids during the 20 year period is calculated to be 1 $lb/ft^2/yr$. Contamination of ground water sources over significant landfill areas at this washout rate is clearly unacceptable. In the second and third cases, 200 and 100 years elapse before leachate reaches groundwater, and leaching of soluble substances occurs at the low loading rate of 0.3×10^{-3} $lb/ft^2/yr$ and 0.7×10^{-3} $lb/ft^2/yr$, respectively. The time for total washout of all soluble solids would be 3000 and 6000 years, respectively. The extent of impact of such a leaching rate would depend on the size of the landfill and the flow of the underground aquifer. For example, for case II, a 1 acre landfill over a small underground water source flowing at one million gallons per year would cause an increase of 2 ppm in the dissolved solids content of the underground water. Most of the 2 ppm increase would be composed of lime and sodium sulfate and sulfite salts. As indicated by Table 5-13, trace elements would comprise a small fraction of the incremental increase, and considering the low solubility of the trace elements, their concentration in the underground water would be at least three orders of magnitude less than the lime, sulfate, and sulfite concentrations, and well below the standard for potable water (see Table 5-9). The rate of leaching can be minimized still further by mixing bentonite with a layer of soil to provide a layer over the filter cake after it has been landfilled to the desired level. The bentonite soil mixture achieves a low permeability of 10^{-9} cm/sec. By contrast, the permeability of silty clay and permeable soils is about 10^{-8} cm/sec, and 10^{-4} cm/sec, respectively. The permeability of the double alkali scrubber cake is 10^{-5} cm/sec, whereas it is about 10^{-4} cm/sec for lime/limestone type scrubber sludges.

Estimated leaching rates can be confirmed by tracking the migration of leachate in the experimental landfill at the reference industrial boiler site. Analyses of this landfill, which contains no seal or barrier other than the native clay silt (permeability of 10^{-6} cm/sec), shows that no leachate has migrated as far as six inches below the disposal layer after the first year of operation. The results and analyses indicate that landfills of untreated scrubber cake can be constructed such that significant adverse impacts will not occur. Moreover, it is conceivable that a completed landfill can be reclaimed for use as a park or farmland, provided a sufficient soil cover is applied and care is exercised not to disrupt the stabilized waste or to permit its migration entry into the terrestrial environment.

The impact of landfilling scrubber cake produced by coal firing is clearly greater than the impact caused by oil firing due to higher concentrations of elements in the cake and larger quantities of cake produced. However, analysis shows that if proper landfill design is employed, utilizing impervious soils, the impact of leaching can be minimized to an insignificant measure whether the scrubber cake orginates from a coal-fired or oil-fired boiler. It is expected that such designs will become mandatory under the rules established by the authority of the Resource Conservation and Recovery Act.

COMPARATIVE SOCIETAL IMPACT

A major societal impact resulting from air pollution and solid waste is aesthetic damage. Emissions of particulate matter and sulfur oxides cause soiling of materials, visibility reduction, and corrosion damage. Solid waste disposal sites are unattractive and generally result in diversion of land use and depreciation of land values.

Effect of Air Emissions--

The primary source of aethestic damage is suspended particulate matter. One obvious esthetic effect of suspended particulates is soiling of property (e.g., homes, automobiles). Soiling results in increased frequency of cleaning and associated economic cost. Particles also cause corrosion of metals. Hygroscopic particles such as sulfate and chloride salts and sulfuric acid aerosol are responsible for accelerating corrosion of metals exposed to the atmosphere. Reliable estimates of the cost of material damage due to pollution are difficult to develop because adequate damage functions are generally not available. However, some preliminary studies have developed functions which may permit crude indications of the potential impact of increased air pollution. Most of these studies have been concerned with the corrosive aspects of suspended particulates.

A regression analysis[33] of the corrosion rate of low carbon steel panels and ambient levels of SO_2 at various sites in the Chicago area indicated high correlation between these variables. Similar high correlation was found between sulfate levels and corrosion rates. The regression equation fitting the data was given as:

$$y = .021\ S + 9.5$$

where y = annual corrosion weight loss (g/100 g panel), S = average SO_2 concentration, $\mu g/m^3$.

Other studies confirm the above findings. Zinc specimens were formed to corrode more rapidly in industrial areas where total suspended particulate levels were highest. Figure 5-9 illustrates the atmosphere of cities with greater concentration of particulates and sulfur oxides produces the greater rates of corrosion.

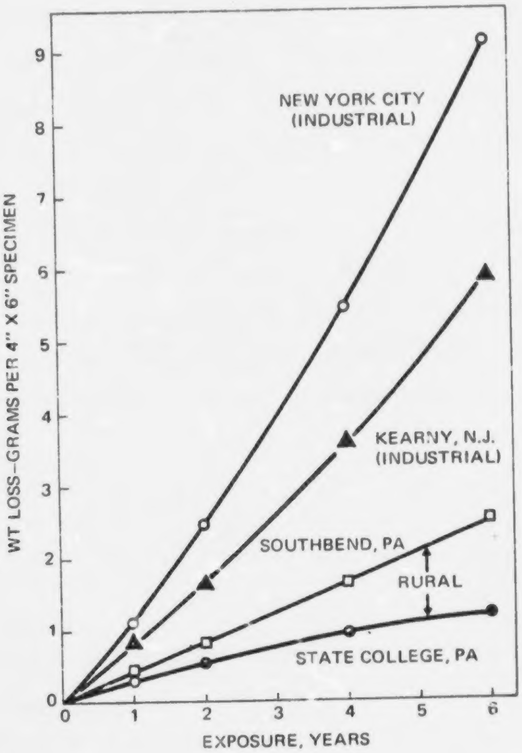


Figure 5-9. Rate of corrosion caused by various levels of TSP and SO_2 in the Atmosphere ,[20].

The relationships developed from the studies above may be used to evaluate in a gross sense the potential impact of industrial boiler emissions on the corrosive properties of the atmosphere. The estimated annual concentration of SO_2 in the vicinity of a cluster of industrial coal-fired boilers is 13 $\mu g/m^3$. (See Table 5-2.) In urban areas where the annual SO_2 levels are 80 $\mu g/m^3$ and TSP is 75 $\mu g/m^3$ (the primary standards), the boiler cluster could be expected to increase the corrosion rate of steel and zinc by about 2.7% and 12% respectively. This impact would be localized within a one or two km range of the industrial cluster, and would be reduced to one forth the effect 5 km away. The expected impact when the industrial boilers are fired with oil is reduced somewhat: the predicted maximum increases in corrosion rates are 1.5% for steel and 8.5% for zinc. It should be noted that the extent of this impact is minor compared to that which occurs in the vicinity of typical non-controlled industrial boilers.

Soiling of structures is particularly noticeable in atmospheres bearing high levels of particulates and sulfur oxides. Particles may soil painted surfaces and cause staining and pitting. Soiling of textiles (clothing, curtains, upholstery) also contributes to direct costs associated with additional cleaning and replacement of damaged property. A soiling cost study[34] of the Washington, D.C. area has determined the cost damage function of residential soiling. The relation was derived by correlating time intervals between cleaning and maintenance with levels of suspended particulates in several areas within the Washington, D.C. area. By translating the frequency of cleaning and maintenance into cost, the following relationship was developed:

$$y = (1.85\ x\ ) - 42$$

where y = cost per capita of soiling damage, x = particulate concentration, $\mu g/m^3$.

This model may be used to estimate roughly the potential impact of controlled boiler emissions on residential soiling damages. The increase in annual TSP levels caused by a cluster of controlled industrial coal fired boilers was estimated to be 7 $\mu g/m^3$. This represents an annual cost increase of $13 per person due to additional cleaning and maintenance. In an area currently experiencing particulate levels equivalent to the federal air quality standard, annual cleaning costs associated with air pollution are \$96 per person. Hence, it seems clear that particulate emissions from a controlled industrial plant complex may cause significant soiling damage, however, these damages are limited to a relatively small area within 1 or 2 km of the industrial complex. According to the emissions test data, the damage occurring in the localized "hotspot" of air pollution is greater (40%) when the controlled boilers are coal-fired as opposed to oil-fired. However, controlled firing of the boilers, whether with coal or oil, results in significantly less soiling damage than would occur from boilers emitting at typical (uncontrolled) levels.

One of the most obvious aesthetic effects of air pollution is decreased visibility. Visibility reduction occurs as a result of absorption and scattering of light by suspended particles. Visibility is affected most dramatically by a narrow segment of the suspended particle size range, from about 0.1 to 1.0 micron. Visual range through suspended particulate matter is given as, [20]:

$$L = \frac{750}{C}$$

where L = visual range in miles, C = concentration of particulates, $\mu g/m^3$. For typical urban concentrations, such as 100 $\mu g/m^3$, the visibility is 7.5 miles, and for rural concentrations such as 30 $\mu g/m^3$, the visibility would be 25 miles.

The visibility model may be applied to estimate the impact of the cluster of industrial boilers on visibility. Figure 5-10 illustrates the variation in particulate concentration downwind of a coal-fired boiler cluster under plume fumigation conditions. The concentration profile is constructed by superimposing the effect of a line of five single plants which are spaced 2 km apart. Because the concentration is non-uniform, application of the visibility model is somewhat awkward. In the vicinity immediately downwind of the plant cluster, visibility would be reduced to about one half an assumed background level of 7.5 miles. However, at a distance 10 miles from the plant cluster, the concentration diminishes to $6 \mu g/m^3$, and visibility would not be impaired significantly. The impact on visibility is not significantly different when the boilers are oil fired. It should be noted that the plume fumigation conditions are short lived,

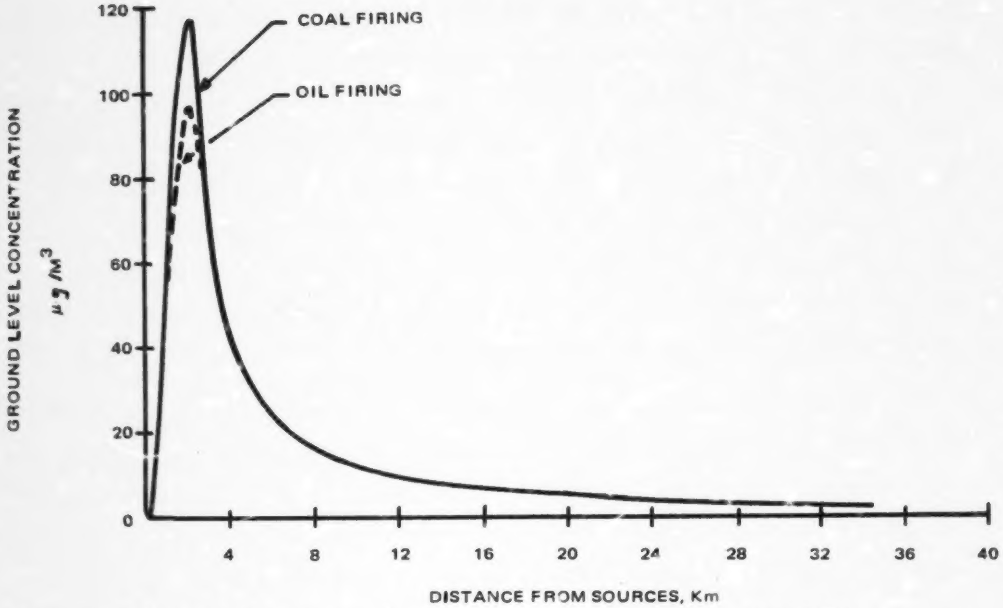


Figure 5-10. Ambient ground level concentration of suspended particulates downwind of cluster of oil or coal-fired industrial boilers.

and that the concentration downwind diminishes dramatically after reaching a peak ground level concentration about 1 km from the end of the cluster. It is also noted that the vertical plume spread is limited, therefore, scattering and absorption of light do not occur throughout the atmosphere, as assumed by the visibility model. Hence, the actual effect on visibility is expected to be appreciably less than a 3.75 mile reduction in visual range, and this effect would be highly localized. Under more typical meteorological conditions, producing peak downwind levels of 29 $\mu g/m^3$ suspended particulate, the visibility reductions occurring from an urban-sited industrial cluster would not be noticeable.

The impact of visibility reductions depend greatly on the characteristics of the existing environment. If an industrial boiler cluster is to be sited in a scenic vista where visibility exceed 50 miles, the impact of atmospheric concentrations which exceed 100 $\mu g/m^3$ could be severe, although highly localized and short-lived. The impact would be essentially the same whether the controlled boilers were burning coal or oil.

Effect of Solid Waste--

The major difference between impacts associated with disposal of scrubber cake from oil firing and coal firing concerns the overall land requirements. Because coal firing produces three times more solid waste than oil burning, diversion of land use for landfills will be more extensive for coal-fired plants. Assuming landfill of waste to a depth of 20 feet, disposal of the scrubber cake from the controlled 10 MW coal-fired boiler will require approximately an acre of land area every 2 years while disposal of the scrubber cake from oil firing will require one acre every 6 years. It may be difficult to secure such land areas in the vicinity of many boiler sites, and the threat of aesthetic degradation and depreciation of land values is a major concern wherever disposal sites are chosen.

COMPARATIVE ECONOMIC IMPACT

The direct economic impacts associated with residuals of fuel combustion involve the costs of damages (or benefits) sustained when the residuals enter the environment. Second order economic impacts associated with the residuals involve the alterations that occur in employment, the tax base, energy prices, income, and land values due to the damages (or benefits) resulting from combustion residuals. The quantification of direct economic impacts involves the difficult task of ascribing economic values to environmental changes. Quantification of second order economic effects are yet more difficult because of gaps in knowledge which make it impossible to determine the complex relationships between cost and the numerous socio-economic factors involved.

A number of ongoing energy related studies are attempting to develop sophisticated economic models which will predict the cost of environmental damages,[2],[5],[41]. The models address the cost of visibility reduction, health effects (morbidity and mortality), and certain second order effects. Utilization of the models requires substantial input data involving regional demography and emission source distributions. The models require further refinement and are currently under continuing development. The data base or scope of the present program did not permit the adaption and utilization of such models.

The comparative extent of the economic impacts resulting from residuals of oil-fired and coal-fired boilers will be proportional to the extent of the comparative environmental damages identified previously. The analyses have shown that the differential impact of emissions from coal firing and oil firing is generally insignificant with the possible exception of some differences which occur in a limited localized area near clusters of boilers. The localized mortality rate for coal firing is about 50% greater than from oil firing, localized soiling damages may be 40% greater from coal firing, localized crop damage may be significantly greater, and land requirements for waste disposal are three times greater for coal firing. The economic cost of these incremental differences will be significant in the limited and affected areas. Medical costs and loss of productivity will be experienced to a greater extent in the area of coal-firing, annual cost of cleanup and maintenance for soiling damages will be about $4 more per person in the most affected area, revenue for crop crop sales will be reduced somewhat, and esthetic blight in the area of landfills will diminish the value of land and activities nearby. The extent of these economic effects is substantially less than that which would be expected from a cluster of either oil firing or coal firing of uncontrolled industrial boilers. Because the significant differences in direct economic impacts occurring from controlled oil-fired and coal-fired boiler emissions are limited to a relatively small area near the source, the total costs of the incremental environmental damages are apt to be insignificant on a regional basis. Consequently, significant incremental second order economic impacts, such as changes in hospital employment, alteration of tax bases, or changes in income would be unnoticeable between controlled oil and coal-fired industrial boilers.

IMPACT ON ENERGY

The comparative effect of environmental residuals from controlled coal combustion versus oil combustion will influence potential restrictions on the production and use of coal or oil. If additional controls are required to assure the environmental acceptability of coal or oil firing in industrial boilers, these requirements will affect the economics of coal utilization and the shaping of energy policy. If it is shown that coal and oil-fired industrial boilers can be controlled adequately at reasonable cost, then policies may be developed to support the use of either of these fossil fuels. Presumably, the use of coal is desirable, given that the associated degree of environmental insult is no worse than that of alternative fuels.

The results of this study tend to support the national energy plan for the intensified utilization of coal. It was shown that both coal and oil-fired industrial boilers may be controlled with reasonably available technology and siting requirements to meet existing environmental standards, and more importantly, that the difference in impact between oil and coal firing in well-controlled boilers is relatively insignificant with the possible exception of effects resulting from a threefold difference in the amount of solid waste generated, as well as potential differences in NO_x emissions levels. The reference boiler of this study was not controlled for NO_x emissions, and the tests showed that coal firing produced two times more NO_x emissions than oil firing. A twofold difference in the uncontrolled NO_x emissions levels could translate to potentially significant differences in ambient levels of photochemical air pollution, and the difference in solid waste generation rates from controlled boilers would lead to greater impacts on land use where waste disposal sites are selected. If additional controls are employed for coal burning plants to mitigate these differences, the cost of coal utilization will increase, and energy policy will be impacted. Whether or not increased coal utilization will be economically attractive will depend on the extent of the incremental control costs for NO_x and solid waste disposal relative to the total cost of coal and oil utilization in boilers.

Table 5-15 illustrates the component costs for operation of a large oil or coal burning boiler. The cost of NO_x emissions control is relatively insignificant compared to SO_x and particulate control. The annualized cost of an FGD and particulate control system may increase the cost of a large boiler by 20 to 30%; the relative increase is still greater for smaller boilers. The annualized cost of FGD and particulate control systems is significantly greater for coal-fired boilers than oil-fired boilers because greater quantities of solid waste (scrubber cake) are generated during

TABLE 5-15. ANNUAL COST OF OPERATING UTILITY BOILERS,[38],[39],[40]

Cost Category	Cost in Mills/Kwhr.	
	Coal	Oil
Capital cost of plant	4.05	3.38
Fuel	3.14	4.04
Fuel Storage	.08	.04
Flue Gas Desulfurization (wet lime/limestone scrubber)	1.6	1.6
Solid Waste Disposal	1.4	.4
NO_x control (low excess air firing and staged combustion)	.03	.03
Operation and Maintenance	.39	.21
TOTAL	10.69	9.70

coal firing. Because landfill waste disposal methods for scrubber cake appear to be environmentally acceptable, additional technology (such as regenerative FGD systems) or special mitigation measures (such as special landfill reclamation techniques) may not be required for either coal or oil combustion. Whatever the comparative extent to which additional controls may be required for oil versus coal-fired boilers, the comparative cost of such controls will probably be relatively minor compared to the overall operating cost of a boiler and other factors affecting the overall costs. The most significant single factor affecting the operating costs of the boiler is the cost of fuel. Any comparison of costs between coal and oil utilization is difficult because of the financial uncertainities associated with future fuel prices. At present, the total generation cost for a coal plant are roughly competitive with those of an oil-fired plant, but may be significantly different if fuel costs change markedly.

Oil prices are determined by a complex set of political and economic considerations. Whether the relative coal prices remain the same, and whether capital will be available to exploit the coal reserves, depends on the existence of a long term market for coal. Unclear and changeable issues such as air pollution regulations, levels of oil imports, natural gas prices, and the cost of capital, create uncertainties for the future coal market.

While the differential impact between combustion in well-controlled coal-fired and oil-fired industrial boilers may pose a relatively minor issue with respect to energy production or utilization, the absolute impacts of fossil fuel combustion may produce serious concerns in the long term. Although the predicted pollutant loadings may meet environmental standards, it is not entirely clear whether the increasing use of fossil fuels may be continued at the forecasted levels of control technology without potential long term environmental damages. If it is found that long term effects of pollution (e.g., trace metals accumulation, lake acidity, land use) are unacceptable, then more stringent environmental regulations can be expected, and it is clear that energy use may be affected. Energy cost will increase with increasing control requirements, possibly to the level where significant social impacts may occur, and other fuel types may become more feasible alternatives.

In conclusion, it appears that the comparative analyses of this study support energy proposals to intensify coal utilization. The combustion of either coal or oil in controlled industrial boilers produces similar environmental effects and the cost associated with mitigating any significant differences in environmental insult are relatively minimal. In supporting the policy for increased coal utilization, the comparative impact of coal versus oil firing carries implications for manv impact sectors associated with the overall coal utilization policy. The impacts are observed among all aspects of energy supply and use, including mining, fuel production, transport, and fuel end use. The affected impact sectors of the social and economic environment include employee demand at development areas, services provided by affected communities, balance of revenues, cost of living, demography, and quality of life. Major impact sectors affected by energy policies in the physical environment include land use by mining operations, water resources and their quality, and ecological systems. The multi-faceted assessment of increased coal utilization policies in terms of the overall energy systems trajectories (e.g., mining-production, etc.) is being conducted in various ongoing studies funded by the federal government. The EPA is currently implementing the CCEA program to coordinate many of these studies into an overall environmental assessment structure. The present study comprises one element of the CCEA program, and focuses specifically on fuel end use by assessing the comparative impact of environmental residuals resulting between oil firing and coal firing in controlled industrial boilers.

SUMMARY

Major general conclusions evolving from the environmental analysis are as follows:

- The difference in environmental insult expected to result between coal and oil combustion emissions from a single controlled 10 MW industrial boiler is insignificant. This is because: 1) there are only slight differences in the emissions levels of the pollutants, or 2) the absolute impact of either fuel use is insignificant.

- The environmental impacts of emissions from a cluster of controlled 10 MW industrial boilers are potentially significant. The impacts include health effects, material damages, and ecological effects from high levels of SO_2, NO_x and suspended particulate matter; health effects and ecological damage due to trace metal accumulation in soils and plants; and esthetic degradation from visibility reduction and waste disposal sites.

- The risk of environmental damage from emissions of controlled industrial boilers, whether oil or coal-fired, is considerably less than the risk posed by emissions from uncontrolled industrial boilers. It should be noted that this finding is based on an exceptional facility. The reference facility is very well run and maintained, and emissions are low.

- The environmental acceptability of a cluster of controlled industrial boiler emissions is more dependent on site specific factors (e.g., background pollution levels, location and number of other sources) than type of fuel utilized. Careful control of the site specific factors can avert potential environmental damages and generally compensate for any differential effects arising between the use of coal or oil.

- With the possible exception of ambient levels of NO , the risk of violating the NAAQS due to operation of clusters of controlled industrial boilers is essentially the same whether the fuel combusted is coal or oil. Based on tests of the reference 10 MW boiler (which was not controlled for NO_x emissions), localized NO_x concentrations produced by coal-firing are estimated to be twice the level of that resulting from oil-firing, and greater than the levels permitted by the NAAQS for 24 hour and one year averaging periods.

- Short term (3 hour and 24 hour averaging times) maximum ambient concentrations present the most significant air pollution problem resulting from operation of controlled industrial boilers. Restrictions imposed by the NAAQS for short term ambient levels would be most constraining to boiler operation in areas where air quality is already only marginally acceptable. Expected long term concentrations arising from boiler emissions would not appear to pose a risk for violation of the NAAQS.

- Coal firing appears to produce a greater enrichment of trace elements in the flue gas desulfurization cake than oil firing produces. However, the scrubber cake resulting from either coal or oil firing contains sufficient amounts of heavy metals and toxic substances to pose difficult waste disposal problems.

The above conclusions are supported by the data summary of Table 5-16 which tabulates estimates of the of the comparative potential impacts resulting from oil firing and coal firing of a clustered configuration of controlled industrial boilers. The impact categories considered include public health, ecology, societal impact, economic impact, and energy. The specific findings with respect to the various impact categories are summarized briefly below.

TABLE 5-16. ESTIMATED ENVIRONMENTAL IMPACTS RESULTING FROM OIL FIRING AND COAL FIRING OF A CLUSTER OF CONTROLLED INDUSTRIAL BOILERS

Impact Category	Analysis Tool	Extent of Impact		Comparative Assessment of Impacts
		Coal Firing	Oil Firing	
Public Health - Mortality	Lundy/Grahn Sulfate Model[5] (regional effects[a])	50 deaths/10^6 persons/yr. in Central U. S.	Same as coal-firing.	No difference
	Lundy/Grahn SO_2 & TSP Model fitted to Lave & Seskin data.	550 deaths/10^6persons/yr. in localized area near boiler cluster.	370 deaths/10^6 persons/yr. in localized area near boiler cluster.	Localized mortality rate from coal-firing is about 50% greater than from oil firing.
Public Health - Morbidity	EPA Health Effects Estimation Model[11]	5% increase in incidence of chronic respiratory disease at threshold level.[b]	Same as coal firing.	No difference
Public Health - effects from plant takeup of trace elements.	40 year deposition of atmospheric trace element loadings and plant concentration ratios.[3]	Produces 30 times increase in endogenous plant concentrations for Mo. Incremental burdens of other elements in plant tissue are from 1/2 to 1/230 the typical plant levels.	Produces 10x increase in endogenous plant levels for Cd and 1.5 x for Mo. Incremental burdens of other elements in plant tissue are from 1/10 to 1/2300 the typical plant levels.	Both oil firing and coal firing could produce elevated levels of a trace element in plant tissue approaching the injurious level to man. Coal produces this increase for Mo and oil produces it for Cd. The effect from other trace element burdens is believed to be insignificant.
Public Health - effects from trace elements in runoff waters.	Application of average sediment burden rates for representative runoff per unit watershed to cumulative soil deposits of metals originating from the boiler emissions.	Se and Mo estimated to exceed background levels for metals in runoff waters. However, levels of all elements are three to seven orders of magnitude less than drinking water standards.	Levels of all elements are three to seven orders of magnitude less than drinking water standards.	Concentration of metals in runoff waters from oil firing expected to be slightly less than that occurring from coal firing. Hazard to human health in either case is remote.
Vegetation (crops)	Empirical data from NO_x laboratory studies[19].	Localized acute leaf damage may occur during short term plume fumigations. Localized growth and yield reductions may be expected over the long term.	Maximum short term concentrations of NO_x expected to be below threshold level for plant damage.	Difference in localized crop damage could be significant, but isolated to about a range of 1 to 3 km from the boiler cluster.
	Empirical data from SO_2 Laboratory Studies[18]	Potential for localized plant damage is remote except in area where SO_2 levels already approach plant damage threshhold (typical in areas where NAAQS are violated).	Same as coal, although slightly more remote chance of leaf damage.	Minor difference.
	Evaluation of acid rain from SO_4 washout.	Insignificant effect on plants due to relatively insignificant levels of suspended sulfates predicted from controlled boilers	Same as coal firing.	No difference.

TABLE 5-16. (Continued)

Impact Category	Analysis Tool	Extent of Impact		Comparative Assessment of Impacts
		Coal Firing	Oil Firing	
	Comparison of expected trace element concentrations in plants with acceptable levels.	Insignificant effect on plants. Possible exception would be localized plant damage due to elevated levels of Mo in plant tissue.	Insignificant effect on plants with possible exception of localized plant damage due to high Cd levels.	Minor difference.
Materials	Corrosion effects. Regression equation from experimental data[33] using SO_2 as determinant, and experimental data for corrosion of zinc in TSP laden atmosphere.	Localized increase in corrosion rate of steel and zinc by 2.7% and 12% respectively (in areas marginally in compliance with NAAQS).	Localized increase in corrosion rate of steel and zinc by 1.5% and 8.5% respectively (in areas marginally in compliance with NAAQS).	Slightly greater corrosion damage expected from coal firing, but difference is localized to relatively small area near boiler cluster.
Property	Soiling cost damage function derived in Washington D.C. area[34].	Annual cost of $13 per person.	Annual of $9 per person.	Localized soiling damages are 40% greater from coal firing.
Visibility	Reduction of visibility based on relationships determined from ambient measurements.[20]	Maximum potential visibility reduction of 4 miles where background visibility is typically urban at 7.5 miles. Effect is extremely localized.	Same as coal-firing.	No difference.
Public Health	Calculation of leaching rates based on permeability data and laboratory analyses of scrubber cake.	Insignificant impact when proper landfill design employed.	Same as coal firing.	No difference.
Drinking water, crops	Calculation of leaching rates based on permeability data and laboratory analyses of scrubber cake.	Insignificant impact when proper landfill design employed.	Same as coal firing.	No difference.
Land use	Calculations of landfill acerage requirements based on 20 ft solid waste layer.	1/4 acre/year Potential reduction in property value near landfill.	1/12 acre/yr. Potential reduction in property value near landfill.	Coal firing requires three times more land use for waste disposal.

a. This application of the Lundy/Grahn model pertains to effects from suspended sulfate. The formation of airborne sulfates is a long range and regionwide problem and is treated by considering emissions levels from industrial boilers throughout the region.

b. The incidence of disease would increase only in those areas where the threshold level of 10 $\mu g/m^3$ sulfate is exceeded regularly.

c. The environmental impact of wastewater from the boiler operation was presumed insignificant. The wastewater is delivered to the municipal sewage treatment facility.

Health Effects--

- Based on the Lundy/Grahn Model for health effects associated with suspended sulfate levels, regional emissions levels from controlled oil or coal-fired industrial boilers would not be expected to cause a significant impact on regional health. Emissions from uncontrolled boilers would result in substantially greater levels of regional suspended sulfate levels, and the associated health effects would be an order of magnitude greater.
- Emissions from clusters of controlled industrial boilers are expected to cause significant adverse health effects in a localized area near the plant cluster. Oil firing would be expected to result in localized health effects about one third less severe than those resulting from coal-firing. The increase in mortality attributable to either well-controlled coal or oil-firing is appreciably less than that associated with uncontrolled industrial boilers emitting higher levels of particulates and SO_x.
- The impact of solid waste generation on health is essentially the same for controlled coal firing and oil firing, provided suitable land disposal techniques are employed to assure minimal leaching rates and migration of trace elements to groundwater and the terrestrial environment.
- Addition of cadmium to a localized environment in the quantities produced by clustered controlled industrial boilers may cause levels of cadmium concentrations in plants approaching levels in-injurious to man. Because cigarettes contain significant cadmium levels, smokers are more apt to achieve thresholds of observable symptoms for cadmium exposure when consuming additional cadmium via the food chain.
- The concentration of metals in runoff waters due to controlled oil-firing is predicted to be slightly less than that occurring from controlled coal firing; in either case, hazard to human health by drinking water is remote.
- Trace element emissions from clusters of controlled industrial boilers may significantly increase local background levels in drinking water, plant tissue, soil, and the atmosphere; however, the expected increases in the levels of such elements are generally several orders of magnitude less than allowable exposure levels. Oil firing is estimated to cause cadmium burdens in plants approaching levels injurious to man, and coal firing may produce plant concentrations of molybdenum which are injurious to cattle.

Ecology--

- The potential for crop damage from either controlled coal firing or oil firing depends greatly on ambient levels of NO_x, SO_2, or trace element soil concentrations. If such levels are presently high, localized plant damage would be expected to occur within a 1 to 2 km range from a controlled boiler cluster. Leaf destruction from SO_2 exposure would be expected to be slightly more severe in the vicinity of a cluster of controlled boilers which are coal-fired as opposed to oil-fired. For boilers uncontrolled for NO_x emissions, plant damage would be expected to be significantly greater in the vicinity of the coal-fired cluster, owing to higher levels of ambient NO_x produced. The likelihood of damage occurring in plants due to emissions of trace elements from either controlled oil or coal firing is remote, with the possible exception of injury due to elevated levels of molybdenum and cadmium in plant tissue resulting from coal firing and oil firing, respectively.

- The effect of emissions from industrial boilers on trace element burdens in plants is greater via soil uptake than by foliar interception. This is because soil concentrations are the result of accumulative long term exposure to boiler emissions whereas foliar exposure is determined by the immediate deposition rate of emissions on the plant surface and the lifetime of the leaf.

- The impact of fossil fuel combustion in controlled oil or coal-fired boilers on plant damage via acid precipitation would be relatively insignificant. The levels of suspended sulfate (the origin of acid rain) would be essentially the same whether the led boilers are coal or oil-fired.

- Measurement and analyses of leaching rates at experimental waste disposal sites indicate that landfills of untreated flue gas desulfurization system scrubber cake can be constructed such that significant adverse impacts will not occur.

Societal--

- The impact of boiler emissions on corrosion in the local area near a cluster of controlled industrial boilers will be significant. The corrosion rate will be slightly greater when the boilers are coal-fired. However, the extent of this overall impact (oil or coal) is minor compared to that which occurs when industrial boilers are uncontrolled.

- The increase in annual TSP and soiling damages in the vicinity of a cluster of controlled industrial boilers results in additional cleaning and maintenance costs about 10 to 15% greater than that already experienced in a typical urban area. The cleaning costs may be slightly greater when the boilers are coal-fired.

- Emissions of particulate matter from controlled industrial boilers will result in visibility reduction. This aesthetic degradation will occur in a localized area near the boiler cluster, and occurs to essentially the same extent whether the boilers are oil or coal-fired.

- Total land disposal requirements for scrubber cake waste generated by controlled coal firing are three times greater than those for for controlled oil firing. Waste disposal of the scrubber wastes may result in significant depreciation of property value and aesthetic degredation in the area of the disposal site. These impacts would be more severe if boilers use coal rather than oil.

Energy--

- At the present time, the comparative assessment of the effects of emissions from controlled oil and coal-fired industrial boilers tends to support the national energy plan for intensified utilization of coal. The fuel choice of oil or coal is a relatively minor issue concerning the environmental acceptibility of controlled industrial boilers; other site specific and plant design factors exert a greater effect on environmental damages. While it was shown that fuel choice caused significant differences in impacts to occur when the boiler is uncontrolled for NO_x emissions, these differences may be mitigated by the addition of NO_x control technologies with minimal overall cost impact.

- As concern for environmental protection increases, the issue may not be whether coal or oil use is more environmentally acceptable, but whether the increasing use of fossil fuels can be continued at the present levels of control technology without potential long term damages. If it is found that long term effects of pollution (e.g., trace metals accumulation, lake acidity from acid rains) from fossil fuel combustion and other sources are environmentally unacceptable, it is clear that energy use may be affected. Energy cost will increase with increasing control requirements, possibly to the level where other cleaner forms of energy become more competitive.

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